INSTITUTE NOTES.

JULY, 1941.

STUDENTS' SECTION (BIRMINGHAM BRANCH)

The Annual General Meeting of the Students' Section (Birmingham Branch) was held on May 22nd, 1941, when the following Officers and Committee were elected:

Chairman	A. L. CUDE.
Vice-Chairman	A. W. PEARCE.
Hon. Secretary and Treasurer	A. N. NISSAN, Ph.D.
Secretary	G. BUXTON.
4th Year Representative	L. GRUNBERG.
3rd Year Representative	M. L. FELLOWES

Seven meetings were held during the Session for 1940–41. Papers presented included "Engine Performance and Development," by H. Fossett (*Associated Ethyl Company*), "The Theory of Surface Catalysis," by S. J. Green, and lectures on their theses and vacation work in Trinidad given by fourth year students. One meeting was devoted to films on various aspects of the petroleum industry.

The average attendance at meetings was twenty-two.

The Section also took an active part in the Mining Society's successful Conversazione held in February last.

ARTHUR W. EASTLAKE,
Honorary Secretary.

No. 2515.

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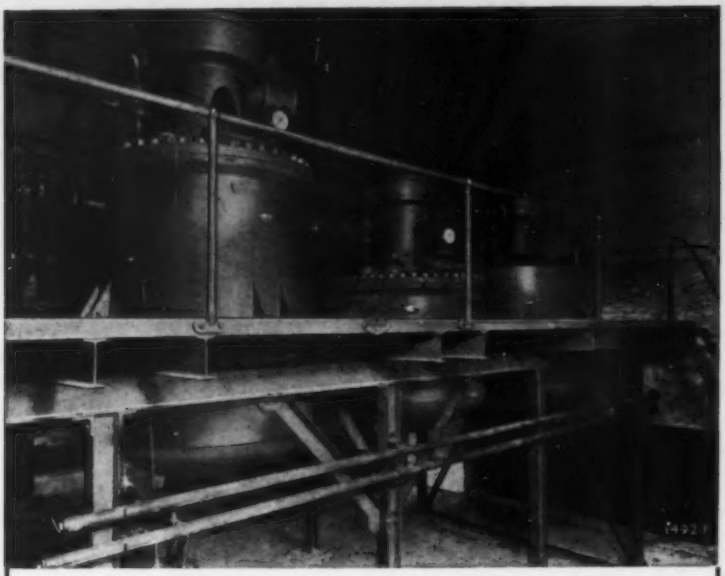

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LORD CADMAN OF SILVERDALE.

(Died 31st May, 1941.)

[*To face p.* 253.

THE LATE LORD CADMAN.

Members of the Institute will have learned with deep regret of the death on 31st May, 1941, of the Rt. Hon. Lord Cadman of Silverdale, G.C.M.G., D.Sc., F.R.S. Lord Cadman was twice President of the Institute, in 1916–17 and in 1935–37 respectively.

A tribute to his memory was paid by the members in London at a General Meeting held on 10th June, when the following Resolution was observed by all members standing in silence :—

> "The Institute of Petroleum has sustained a serious loss by the death of Lord Cadman and we, the members of the Institute, wish to record in our Proceedings our appreciation of his many qualities.
>
> "John Cadman was a man of wide culture and great ability, and his experience and sound judgement led him to take a broad view on all matters of policy connected with this Institute.
>
> "It was always easy to approach Lord Cadman on any problem, for he was invariably courteous and helpful; and no trouble was too great for him in any matter which concerned the welfare of the Institute of Petroleum or its members.
>
> "Lord Cadman reached the great position he held by his talent and ability, but with these qualities were joined a charm of manner which endeared him to those who were so fortunate as to enjoy his friendship.
>
> "Our deepest sympathy is extended to Lady Cadman and the members of his family."

At the Memorial Service held at Westminster Abbey on 18th June the Institute was represented by the President.

It is intended to publish in a future *Journal* an account of Lord Cadman's long and brilliant career and his association with the petroleum industry and the Institute. In the meantime, the Honorary Editor has received the following tributes:

From The President, Professor A. W. Nash.

The death of Lord Cadman came as a great shock to those who knew him well and to those whom he had befriended, for he made friends easily in every walk of life, from the exalted to the most humble. Indeed, the great charm of his nature was that he was the same John Cadman to all, no matter what their station.

The writer had many opportunities of meeting Lord Cadman in widely different circumstances, and no matter whether it was amongst Government officials, scientists, colliery men, oil men, or business men, his analytical mind always showed to advantage, particularly when difficulties presented themselves.

There can be no doubt that he owed much of his success in life to that abounding energy which he displayed in anything he undertook, and the

old proverb, " if you want work done, go to the man who is already fully occupied," was well exemplified by him.

John Cadman had many friends, but I cannot recall that he had a single enemy during the long period I knew him, for although he was never afraid to doubt, he always retained the disposition to believe.

Lord Cadman had a catholicity of thought and vision which showed great depth of mind and learning, and it is given to very few indeed to find success first as a Government Administrator, then as a University Professor, and finally as a leader of industry, as he did. In this latter respect he won admiration of men of science for his unceasing advocacy of the application of science to industry, and his reward was to be found in the success of the Sunbury Research Station, for the creation of which he was largely responsible.

By the old students of the Mining Department of the University of Birmingham Lord Cadman will be remembered with respect and gratitude for his kindly interest in their welfare. This was proved by the way in which they used to gather at the Annual Dinners of the University Mining Society when it was known that he would be present.

Of the many good traits in John Cadman's character, the one which most impressed itself upon the writer was the fact that he always respected the considered opinion of others even although it might clash with his own. A true sign of greatness.

A distinguished character, which held the admiration, esteem and regard of all who knew him, has passed on, but John Cadman's engaging personality will remain with us all so long as memory survives.

From Sir Thomas H. Holland, K.C.S.I., K.C.I.E., F.R.S.

Professor John Cadman was one of the group of twenty-nine, described in the original Articles of Association, dated 8th April 1914, as " the first Members of the Institution "; and in technical qualifications he was the only one among us who could be regarded in the complete sense as a " petroleum technologist ". Quite appropriately therefore, he was chosen at the annual meeting in 1916 to follow the Founder as our second President. But he was far more than a technologist: on his broad technical foundation he qualified to succeed Lord Greenway as Chairman of the Anglo-Persian Oil Company, and thereafter added strength with symmetry to a great commercial industry by establishing within its structure a research organisation which has contributed substantially to the body of pure science in the related branches of chemistry, physics, geology and geophysics.

Lord Cadman's success in developing the Company was due also to his ability to look at the growing structure from outside, and so to see the parts in true perspective; to attract the best among specialist workers; to give them freedom of action and then generous appreciation of their efforts. And these measures, designed to secure the efficient health of the machine within, obtained their commercial value because of his wise " foreign " policy—his generous regard for the rights of competitors and his well-known loyalty to understandings with them. He, more than any single person, was instrumental in abolishing the " aggressive " commercial

policy to which, during the earlier years of this century, some of the larger oil organisations tended, for he recognised how seriously this would lead ultimately to the disadvantage of all of them, by failure to apply technological science to their full development of the oilfield resources. With all his heavy responsibilities outside, Lord Cadman found time to lend his unusual abilities and sane judgment to the smaller affairs of the Institute, after as well as during his term of office as President. All who worked with him from our foundation, twenty-seven years ago, must feel with his death that we have lost a very valuable and trusted personal friend. Probably my contact with him goes back further than that of any other member, except Mr. Cunningham Craig; for he was specially helpful to me as a member of the Royal Commission on Navy Fuel before the last war; that was after and largely because of the warm discussion which we had had about the suitability of petroleum technology for a university degree course—a discussion in which subsequent experience showed his judgment to be the sounder of the two! His activities were so varied that it will be difficult to summarise the many ways in which he contributed to the healthy growth of the oil industry—its bearing on education; its reaction on science and technology; its relation to other fuel industries; its national and even international value; its support of this Institute.

From Sir William Fraser, C.B.E.

I began a quarter of a century's close association with Lord Cadman in 1916. He was then about to relinquish his work in connection with gas warfare and to devote himself to petroleum. Commencing by directing the Petroleum Executive, he was to proceed to the Chairmanship of the Inter-Allied Petroleum Council, the Board of Anglo-Iranian Oil Company, the Chairmanship of that Company and the host of other activities which brought him fame. He was then Professor John Cadman, and had not yet received the many honours which subsequently rewarded his work and character. Yet, when numerous distinctions had fallen to him and he had become a figure of international repute, he remained essentially the same John Cadman that he was when I first came into close touch with him. His character was unspoiled, his charm of manner never left him, his kindliness and consideration were constant. He was not "all things to all men," but one man—and that a very human one—to all.

John Cadman entered the world of petroleum at one of its most critical and momentous periods. After the war of 1914–1918, the industry was on the threshold of tremendous developments. The mass-produced motor car, the aeroplane, the use of oil as ships' bunkers, the diesel engine on land and in ships were each to make demands on the petroleum industry. Science was to revolutionize the search for new fields, the drilling of wells and the entire technique of petroleum refining. Vast new fields were to be discovered to falsify prophecies of early exhaustion of reserves of crude. The ruthless competitive methods of pre-war days had, if the industry was to develop sanely and without waste, to be replaced by the guiding principle of co-operation.

All this, John Cadman foresaw in that wide vision which so distinguished him; and he shaped his efforts and those of the Company to further these

aims. He was amongst the leading exponents of two courses of action for the petroleum industry—the application of science to all its operations and the development of a co-operative spirit among all the individuals and organizations, of whatever nationality, having influence in its control.

The measure of success which, together with others of a like kind, he achieved, was amply demonstrated during the years when potential production outstripped all possible demand and when production let loose would have put an end to orderly development, to say nothing of ruining thousands of the smaller participants in the industry, as well as some of the larger, and leaving the world the poorer by the dissipation of an irreplaceable natural asset.

To John Cadman the potentialities of science were limitless. He never looked merely one or two years ahead; he was not satisfied with a small measure of progress. He had his mind always on an ideal; and although he welcomed any progress towards it, he never rested content, but regarded the completion of one stage solely as a stimulus to start on the next. He gave a great impetus to scientific development in many spheres of industrial activity in addition to petroleum. He had clear-cut views on coal and, indeed, on all types of fuel. When ships were to be constructed for the Anglo-Iranian Oil Company's fleet, he needed assurance that every scientific aid had been invoked in hull design and that the completed vessels would be the best that science and engineering skill could contrive.

It was, indeed, a well-deserved tribute that Professor John Cadman, D.Sc., became Lord Cadman, F.R.S.

From T. Dewhurst, Esq.

In the late Lord Cadman a rare and even unique personality has passed on. Even his negative qualities were remarkable, and included a complete absence of pretence and pose, freedom from turbulence and impatience and the avoidance of any but the most simple language in which to express his thoughts.

These negative traits were a mask to his positive qualities. His quiet manner concealed immense driving power, his simple language hid vast stores of knowledge and wisdom, his simplicity veiled gifts of diplomacy of a high order and his geniality and hospitality a keen appreciation of men and affairs.

His insight into human nature had an X-ray quality which gave him an instinctive knowledge of the wise course to adopt in any situation and enabled him to smooth over difficulties and remove causes of friction. In carrying out his manifold duties this quality was invaluable. For example, as chairman of a Royal Commission he would instantly and unerringly pick out the man or men who possessed the fundamental scientific and technical knowledge of the subject under reference, and such men received his complete confidence, warm friendship and generous praise.

His hospitality was princely, and enabled him to break down the barriers between various classes of men. Reference can only be made here to the remarkable gatherings at the large circular table that was made for Disraeli so that all present could be equal. Those who were fortunate enough to have been his guests will always treasure the experience.

A volume would be needed to do justice to his services and achievements in various spheres of activity. In academic life, in science and technology, in the coal and oil industries and in Government service, records exist that bear the impress of his powers. The highest testimony to the value of these achievements was provided by the high positions he held, and by the honours that were showered on him by Governments, Universities, and Scientific and Technical Societies.

In his plans he showed depth of knowledge, width of outlook and length of vision. A big, simple and boldly conceived scheme of his would be regarded by some horse-shy critics as unnecessary, while others would mistake size for grandiosity. After his quiet persistence had won through, and the scheme was in being, the critics would realize their mistakes and also that wise planning such as his was one of the rarest of gifts.

Great services rendered to his country deserve a special tribute. In times of peace he served on many Government commissions and committees, and was Chairman of several of them, and the reports bear the impress of his qualities. But his services were even greater in times of war. Early in 1917 there was a serious shortage of petroleum products for the Navy, while Sir Douglas Haig had only a few days' supply. Professor Cadman was called in and became Director of the Petroleum Executive and, later, Chairman of the International Allied Petroleum Council. He was responsible to the War Cabinet through the late Lord Long, who paid the following tribute to his work. "The success which happily attended our administration is entirely due to his great ability, wonderful industry, and unsurpassed knowledge of oil questions. . . . In all the long list of services rendered by both men and women, which contributed to the ultimate victory, there is none which stands higher than the work which Sir John Cadman did." For these services he was made K.C.M.G., Officier Légion d'Honneur and Knight Commander of the Crown of Italy.

After some forty years of strenuous activity in many spheres, Lord Cadman had earned the right to peaceful sunset years, but he was to know no Indian summer, for when the Nazi war started he again placed his knowledge, experience and abilities at the disposal of the Government, and finally spent himself in the country's service.

Many men received from the late Lord Cadman more kindness and sympathetic understanding than they received from any other man. Of the many memorials to him, none will be more fitting than the thoughts and feelings of affection and gratitude in the minds and hearts of his fellows, and this memorial will endure until the last of them has passed away.

"Our greatest yet with least pretence,
Great in council and in war,
A leading captain of his time,
Rich in saving common-sense,
And, as the greatest only are,
In his simplicity sublime."

From Dr. A. E. Dunstan.

As it is proposed to publish in the *Journal* at a later date a biography of the late Lord Cadman, it is rather the intention of this short tribute to

throw into relief his achievements as a man of science, and it is more than likely that it is just this aspect of his life that Lord Cadman would have wished emphasized.

After more than twenty-five years of close association with him, it is apparent that the scientific approach to industrial problems had assumed an overwhelming importance. In all the wide gamut of the petroleum industry, from the initial geophysical exploration, the geological demarcation of oil-bearing formations, the technology of drilling, the corrosion of pipe-lines and plant and ships to the chemistry of refining processes, his fluid and prehensile mind was fully occupied and extended. There was probably no one man of our epoch with the same encyclopaedic knowledge and, what is more important, the same wide and active sympathy with those who were associated with him as his scientific colleagues.

In his younger days Cadman was primarily a " coal " man. At the age of twenty-six he was appointed H.M. Inspector of Mines for East Scotland, and very shortly after was seconded to Trinidad as Government mining engineer. . It was in this position that he encountered the multitudinous problems of the petroleum industry. Returning to England in 1907, he became professor of mining in the University of Birmingham, a post he held for thirteen years, during which time he founded the first school of petroleum technology to be established in the Empire, and was Professor Emeritus at the time of his death. It was in Birmingham that his close collaboration with his old friend, the late Prof. J. S. Haldane, began, and a fruitful series of investigations into various mine hazards was accomplished. In the War of 1914–18 he was intimately concerned in the problems of trench warfare and of gas protection. Ultimately he was made director of the Petroleum Executive and chairman of the Inter-Allied Petroleum Council. He co-ordinated all oil supplies both for the United Kingdom and the Allies. During these busy years, and for long afterwards, he retained his interest in the scientific and technical aspects of industry, served on innumerable commissions and committees and occupied the presidential chairs of the Institute of Petroleum, the Institute of Fuel and the Institute of Mining Engineers.

He received the medals awarded by the latter two bodies. He served on the Advisory Council of the Department of Scientific and Industrial Research of the Privy Council, the Safety in Mines Research Board, the Coal Advisory Council and the Prime Minister's Economic Advisory Council. He was a member of the Fuel Research Board from 1923 until his death, except for a short break of four years. During the time he was a member of the Board he was intensely interested in the work and took a prominent part in the discussions of the Board. Although he was so intimately associated with oil, his association with the coal industry had left him with real sympathy with the subject, and he never hesitated to use his influence to further the scientific application of coal. He continually advocated the complete gasification of coal so that cheap gas could be made accessible in large volumes in Great Britain. He also took a great interest in the production of motor spirit from coal by the hydrogenation process. The coping-stone of his scientific career was placed only last year by his election to the Fellowship of the Royal Society.

As one of his oldest colleagues, the writer wished to stress Cadman's

perpetual insistence that no industry can flourish that is not soundly based on truly scientific foundations. In the Anglo-Iranian Oil Company he fostered research. He was responsible for the creation of the largest petroleum station in the Empire, and one that will bear every comparison with corresponding organizations abroad. He was deeply sensible of the latest and best scientific advice. He supplemented the efforts of his own staff with those of highly skilled and eminent advisers. He continually visited the laboratories, and took the keenest interest in the welfare and well-being of his staff. In return he was rewarded by a constant stream of invention, discovery and development.

MOLAL VOLUME RELATIONSHIPS AMONG ALIPHATIC HYDROCARBONS AT THEIR BOILING POINTS.*

By Gustav Egloff and Robert C. Kuder.

PART I. RELATIONSHIPS BETWEEN MOLAL VOLUME AND MOLECULAR STRUCTURE.

A. Introduction.

Regularities in molal volume relationships among homologous series of organic liquids were first studied by Kopp.[6] He pointed out that at the boiling point the molal volume was an additive function, its value in the case of hydrocarbons varying linearly with the number of carbon atoms in the molecule.

Other later investigators have also used the molal volume additively, calculating molal volumes of compounds from the sums of the atomic volumes of the component elements. However, as the amount of more accurate density data has grown, it has become increasingly evident that linear relationships between molal volume and molecular weight do not represent the experimental data with a sufficient degree of accuracy. Le Bas [7] realized the inadequacy of linear equations, and in 1915 proposed for *n*-alkanes a formula of the type :

$$V = an^2 + bn + c$$

in which V is the molal volume at the boiling point and n is the number of carbon atoms in the molecule, whilst a, b, and c are constants. Even this parabolic equation was valid for only the higher members of the series ($n > 5$).

Another objection to Kopp's generalizations is that isomers do not have identical molal volumes. Constitutive effects, such as branching of the carbon chain or position of the double or triple bonds, are clearly revealed in the light of present data.

In Part I of this paper, a correlation of the molal volumes of aliphatic hydrocarbons at their boiling points and the number of carbon atoms in the molecule will be made for several homologous series. The boiling point was chosen as a standard reference point, since this temperature permits comparisons to be made at approximately equal fractions of the critical temperatures.

B. Selection of the Data.

The boiling point and density data used were the most probable values given by Egloff,[4] except for a few changes and additions necessitated by

* Presented before the Division of Physical Chemistry of the American Chemical Society Detroit Meeting, 9–13th September, 1940.

recently published data. In Table I, column 2, appear the values which differ from those of Egloff, and the reason for the change or addition.

TABLE I.

Compound.	D_4^{20}.	Reason.
2 : 2-Dimethylpropane	0·613	0·613 given by Hoog, Smittenberg, and Visser: R–51–S2, *II^e Congres Mondial du Petrol, Paris*, June, 1937.
3 : 3-Dimethylhexane .	0·7095	0·7107 given by Marker and Oakwood, *J. Amer. chem. Soc.*, 1938, **60**, 2598.
3-Ethylheptane . .	0·7266	0·7272 given by Whitmore and Orem, *ibid.*, 1938, **60**, 2573.
2-Methyloctane . .	0·7124	0·7132, *ibid.*
2 : 2-Dimethylheptane	0·7105 (b. pt. $_{760}$, 130·4)	0·7105 and 130·4 given by Marker and Oakwood, *loc. cit.*
2 : 5-Dimethylheptane	0·7134	Conversion of S_{20}^{20} into D_4^{20}.
2 : 6-Dimethylheptane	0·7094	0·70949 given by White, Rose, Jr. Calingaert, and Soroos, *J. Res. Nat. Bur. Standards*, 1939, **22**, 315.
3 : 3-Dimethylheptane	0·7279	0·7254 given by Marker and Oakwood *loc. cit*
3 : 3-Dimethyloctane	0·7390 (b. pt. $_{760}$, 161·2)	0·7390 and 161·2, *ibid.*
2 : 4-Dimethyloctane .	0·7246	Conversion of S_{20}^{20} into D_4^{20}.
Ethene . . .	$0·5676^{-103·4}$	Correction of misprint.

The densities of the first four *n*-alkanes are known at their boiling points. The densities of the remaining members of the series must be extrapolated to the boiling points. For *n*-alkanes containing thirteen or more carbon atoms, density data are so few and the boiling points so high that it is impractical to extrapolate the densities to the boiling points. However, from *n*-pentane to *n*-dodecane temperature coefficients of density are valid over sufficient temperature ranges so that densities may be calculated at the boiling points with extrapolations varying from only 0·71° in the case of *n*-nonane to 18·8° in the case *n*-hexane.

Of forty-two branched-chain alkanes considered, only four have density determinations over extended temperature ranges. The densities at the boiling points of three of these (2-methylpropane, 2 : 2-dimethylpentane, and 2 : 2 : 4-trimethylpentane) may be interpolated accurately from the experimental data; the density at the boiling point of the other (3-ethylpentane) may be calculated from the published temperature coefficients[4] requiring an extrapolation of only 3·3°.

For the thirty-eight remaining branched-chain alkanes, the temperature coefficients of density are either not known or are not determined over temperature ranges sufficiently wide to extrapolate the densities to the boiling points. A plot of density against temperature showed that over the ranges which have been investigated the curves for branched-chain alkanes are approximately parallel to the curves for the corresponding *n*-alkanes. Therefore the densities of the remaining branched-chain alkanes were extrapolated to their respective boiling points using the same temperature coefficients as for the corresponding straight-chain isomers. Since the extrapolations involved vary from about 40° for hexanes to nearly 150° for decanes, it is probable that the error introduced by using

parabolic curves parallel to the straight-chain curves is not as great as that which would be introduced if straight lines determined by temperatures only 5–20° apart were used.

The densities of the first three 1-alkenes have been determined over extended temperature ranges, and the densities at the boiling points are known.[4] The density of pentene-1 and of hexene-1 at their respective boiling points were determined by graphical extrapolation. Above hexene-1 the data do not warrant extrapolation.

The densities at the respective boiling points of the first three 1-alkynes are also reported,[4] but the density of butyne-1 at its boiling point is obviously so out of line that it was discarded from the series. The density of pentyne-1 at its boiling point was determined from the calculated temperature coefficient,[4] and the boiling-point densities of the next three members of the series were obtained by graphical extrapolation.

It is evident from the above discussion that much more experimental data on densities near the boiling point would be very helpful in studies of this type.

C. The Empirical Equation.

The boiling points of aliphatic hydrocarbons can be expressed accurately [5] by an equation of the type

$$T = a' \log(n + b') + k'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the constant b' has a value of 4·4. It was considered desirable to develop an equation for V, the molal volume at the boiling point, as a function of $(n + 4{\cdot}4)$, so that a simple relationship would exist between the boiling-point equation and the molal-volume equation. Graphical analysis of the data for n-alkanes showed that a formula of the type

$$V = a(n + 4{\cdot}4)^c + k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

was required. In the logarithmic form,

$$\log (V - k) = \log a + c \log (n + 4{\cdot}4). \quad . \quad . \quad . \quad (3)$$

the constants a, c, and k were evaluated for n-alkanes by the method of least squares.* Only the first ten members of the n-alkane series were used in fitting the equation, since there are no branched-chain alkanes nor alkenes or alkynes of more than ten carbon atoms with data suitable for comparison with the n-alkanes, and since, further, the data for the higher members of the n-alkane series itself are unreliable, as pointed out above.

The constants obtained for n-alkanes are $a = 7{\cdot}9990$, $c = 1{\cdot}32243$, and $k = 37{\cdot}00$. Table II shows the agreement between the calculated and the observed values. The agreement is good (deviations less than 0·5 ml./mol) for all members with the exception of ethane, which has a calculated value 1·11 ml. too high. The mean deviation for all ten members is 0·30 ml./mol (0·20 ml./mol, excluding ethane).

For homologous series of branched-chain alkanes the data may be represented by keeping c and k the same as for n-alkanes, whilst a is adjusted for each series. The constant a was evaluated for eleven homolo-

* An approximate value of k was first chosen graphically, and the corresponding approximate values of a and c calculated. The more exact values of a, c, and k were then found by application of Taylor's expansion.

gous series of branched-chain alkanes; the calculated and observed values of the molal volumes are shown in Tables III to XIII. The mean deviation for the forty-two branched-chain alkanes considered is 0·41 ml./mol; for all fifty-two alkanes, 0·39 ml./mol.

For alkenes and alkynes, k was kept the same as for alkanes, but $a = 6{\cdot}5807$ and $c = 1{\cdot}38856$ for 1-alkenes, whilst $a = 5{\cdot}3171$ and $c = 1{\cdot}45121$ for 1-alkynes. The calculated and observed values for the first five 1-alkenes are shown in Table XIV; the mean deviation is 0·21 ml./mol. The calculated and observed values of the first seven 1-alkynes are shown in Table XV; the mean deviation is 0·50 ml./mol.

In Table XVI is given a summary of the preceding fourteen tables. The mean deviation for all the sixty-three aliphatic hydrocarbons considered is 0·39 ml./mol. This agreement appears to be good when it is remembered that most of the "observed" molal volumes are calculated from extrapolated density values.

TABLE II.

n-Alkanes.

$V = 7{\cdot}9990(n + 4{\cdot}4)^{1{\cdot}22243} - 37{\cdot}00.$

n.	V obs.	V calc.	ΔV.
1	37·83	37·40	−0·43
2	55·03	56·14	1·11
3	75·80	75·86	0·06
4	96·59	96·46	−0·13
5	118·09	117·86	−0·23
6	140·07	140·01	−0·06
7	163·10	162·86	−0·24
8	186·64	186·37	−0·27
9	210·42	210·49	0·07
10	234·86	235·21	0·35

TABLE III.

2-Methylalkanes.

$V = 7{\cdot}9715(n + 4{\cdot}4)^{1{\cdot}22243} - 37{\cdot}00.$

n.	V obs.	V calc.	ΔV
5	117·81	117·33	−0·48
6	139·03	139·39	0·36
7	162·34	162·17	−0·17
8	185·88	185·59	−0·29
9	210·07	209·63	−0·44
10	233·24	234·26	1·02

TABLE IV.

3-Methylalkanes.

$V = 7{\cdot}8983(n + 4{\cdot}4)^{1{\cdot}22243} - 37{\cdot}00.$

n.	V obs.	V calc.	ΔV.
6	137·90	137·77	−0·13
7	159·91	160·34	0·43
8	183·99	183·54	−0·45
9	207·46	207·36	−0·10
10	231·53	231·77	0·24

TABLE V.

3-Ethylalkanes.

$V = 7{\cdot}8357(n + 4{\cdot}4)^{1{\cdot}22143} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV.
7	158·64	158·77	0·13
8	182·06	181·80	−0·26
9	205·30	205·43	0·13

TABLE VI.

2 : 2-Dimethylalkanes.

$V = 7{\cdot}9088(n + 4{\cdot}4)^{1{\cdot}22143} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV.
5	115·82	116·11	0·29
6	138·41	138·00	−0·41
7	161·14	160·60	−0·54
8	183·85	183·84	−0·01
9	207·02	207·69	0·67

TABLE VII.

2 : 2′-Dimethylalkanes.

$V = 7{\cdot}9345(n + 4{\cdot}4)^{1{\cdot}22143} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV.
7	161·77	161·24	−0·53
8	184·65	184·56	−0·09
9	208·43	208·49	0·06
10	232·44	233·00	0·56

TABLE VIII.

2 : 3-Dimethylalkanes.

$V = 7{\cdot}8358(n + 4{\cdot}4)^{1{\cdot}22143} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV.
6	137·30	136·39	−0·91
7	158·32	158·78	0·46
8	181·19	181·80	0·61
9	205·59	205·43	−0·16

TABLE IX.

2 : 3′-Dimethylalkanes.

$V = 7{\cdot}8937(n + 4{\cdot}4)^{1{\cdot}22143} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV.
8	183·26	183·41	0·15
9	207·16	207·22	0·06
10	231·83	231·61	−0·22

TABLE X.

2 : 4- *and* 2 : 5-*Dimethylalkanes.*

$V = 7{\cdot}8524(n + 4{\cdot}4)^{1{\cdot}032143} - 37{\cdot}00.$

n.	Compound.	*V* obs.	*V* calc.	ΔV
9	2 : 4-	205·99	205·94	−0·05
10	2 : 4-	230·82	230·21	−0·61
10	2 : 5-	229·55	230·21	0·66

TABLE XI.

3 : 3-*Dimethylalkanes.*

$V = 7{\cdot}7815(n + 4{\cdot}4)^{1{\cdot}032143} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV.
7	157·79	157·42	−0·37
8	180·82	180·28	−0·54
9	203·22	203·75	0·53
10	227·42	227·80	0·38

TABLE XII.

2 : 2 : 3-*Trimethylalkanes.*

$V = 7{\cdot}7516(n + 4{\cdot}4)^{1{\cdot}032143} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV
7	157·37	156·67	−0·70
8	178·75	179·45	0·70

TABLE XIII.

2 : 2 : 2′-*Trimethylalkanes.*

$V = 7{\cdot}8665(n + 4{\cdot}4)^{1{\cdot}032143} - 37{\cdot}00$

n.	*V* obs.	*V* calc.	ΔV.
8	183·88	182·66	−1·22
9	206·26	206·38	0·12
10	229·59	230·69	1·10

TABLE XIV.

1-*Alkenes.*

$V = 6{\cdot}5807(n + 4{\cdot}4)^{1{\cdot}032156} - 37{\cdot}00.$

n.	*V* obs.	*V* calc.	ΔV.
2	49·42	49·64	0·22
3	68·93	68·99	0·06
4	89·69	89·38	−0·31
5	110·95	110·75	−0·20
6	132·76	133·01	0·25

TABLE XV.

1-Alkynes.

$V = 5{\cdot}3171(n + 4{\cdot}4)^{1{\cdot}45121} - 37{\cdot}00.$

n.	V obs.	V calc.	ΔV.
2	41·91	41·64	−0·27
3	59·67	60·08	0·41
4	—	79·68	—
5	101·39	100·37	−1·02
6	122·73	122·08	−0·65
7	144·92	144·75	−0·17
8	167·85	168·34	0·49

TABLE XVI.

Values of a and c for Aliphatic Hydrocarbons.

Series.	a.	c.	Mean deviation.
n-Alkanes	7·9990	1·32243	0·30
2-Methylalkanes	7·9715	,,	0·46
3-Methylalkanes	7·8983	,,	0·27
3-Ethylalkanes	7·8357	,,	0·17
2 : 2-Dimethylalkanes	7·9088	,,	0·38
2 : 2′-Dimethylalkanes	7·9345	,,	0·31
2 : 3-Dimethylalkanes	7·8358	,,	0·54
2 : 3′-Dimethylalkanes	7·8937	,,	0·14
2 : 4-, 2 : 5-Dimethylalkanes	7·8524	,,	0·44
3 : 3-Dimethylalkanes	7·7815	,,	0·46
2 : 2 : 3-Trimethylalkanes	7·7516	,,	0·70
2 : 2 : 2′-Trimethylalkanes	7·8665	,,	0·81
1-Alkenes	6·5807	1·38856	0·21
1-Alkynes	5·1371	1·45121	0·50

D. THE EFFECT OF MOLECULAR STRUCTURE ON MOLAL VOLUME.

If the various homologous series of alkanes are arranged in order according to the magnitude of the constant a, equation (2), some interesting relationships are evident (see Table XVII).

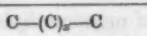
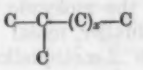
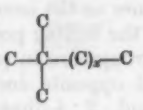
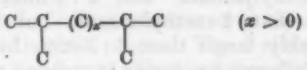
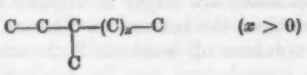
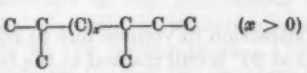
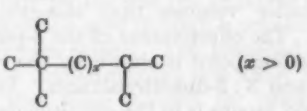
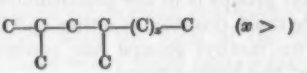
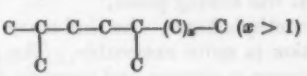
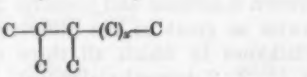
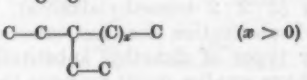
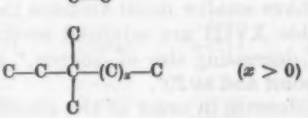
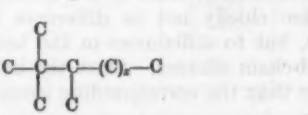
Among isomeric alkanes a straight-chain compound always has a larger molal volume at the boiling point than any branched-chain compound. The sole exception to this generalization is 2-methylpropane (not included in Table III), which has a molal volume of 97·44 ml., whilst n-butane has a molal volume of 96·59 ml. The difference in molal volume between a straight-chain alkane and any isomer is not constant within each series, but increases as the molecular weight increases, although not always regularly if calculated from the observed values. If V_1 denotes the calculated volume of a given n-alkane, and V_2 the calculated volume of an isomer, then, from equation (2),

$$V_1 - V_2 = (a_1 - a_2)\,(n + 4{\cdot}4)^c,$$

where a_1 and a_2 are, respectively, the values of a for n-alkanes and for the homologous series of which the isomer is a member.

TABLE XVII.

Alkanes.

a.	Type of substitution.	Carbon skeleton.
7·9990	Normal	
7·9715	2-Me-	
7·9345	2 : 2-Me_2-	
7·9088	2 : 2′-Me_2-	 ($x > 0$)
7·8983	3-Me-	 ($x > 0$)
7·8937	2 : 3′-Me_2-	 ($x > 0$)
7·8665	2 : 2 : 2′-Me_3-	 ($x > 0$)
7·8524	2 : 4-Me_2-	 ($x >$)
7·8524	2 : 5-Me_2-	 ($x > 1$)
7·8358	2 : 3-Me_2-	
7·8357	3-Et-	 ($x > 0$)
7·7815	3 : 3-Me_2-	 ($x > 0$)
7·7516	2 : 2 : 3-Me_3-	

The effects of branching at the boiling point are in marked contrast with the effects at 20°, which have been pointed out previously.[1, 2, 3] At 20° substitution in the 2-position always increases the molal volume over that of the normal isomer, unless the adjacent 3-position is also substituted.

At the boiling points of monomethylalkanes the molal volume decreases the nearer the centre of the molecule the methyl group is situated—*i.e.*, 3-methylalkanes have smaller molal volumes than isomeric 2-methylalkanes. However, at 20° 2-methylalkanes are about as much larger than the corresponding *n*-alkanes as the isomeric 3-alkanes are smaller.

In dimethylalkanes at the boiling point the diminution of volume is the least when the methyl groups are in penultimate positions, either on the same carbon atom or at opposite ends of the molecule. For example, 2 : 2-dimethylpentane and 2 : 4-dimethylpentane have smaller molal volumes than 2-methylhexane, but larger than 3-methylhexane, and considerably larger than 3 : 3-dimethylpentane. However, at 20° 2 : 2-dimethylalkanes are larger in volume than isomeric 2-methylalkanes, and larger yet than the isomeric *n*-alkanes. Both at the boiling point and at 20° the volumes of isomeric 2 : 2- and 2 : 2′-dimethylalkanes are nearly equal.

The contraction in volume due to adjacent dimethyl substitution which is noticed at 20° is still marked at the boiling point. 2 : 3-Dimethylalkanes have smaller volumes than isomeric 2 : 2, 2 : 2′-, and 2 : 3′-dimethylalkanes. The effectiveness of the 3-position in lowering the molal volume at the boiling point is shown by the relatively small volumes of 3-ethylalkanes and 3 : 3-dimethylalkanes. In dimethylalkanes in which one of the methyl groups is in the penultimate position and the other is in neither the 2- nor the 3-position at either end of the molecule, the relative position of the two methyl groups has comparatively little effect on the molal volume at the boiling point.

In trimethylalkanes the influence of penultimate and of adjacent substitution is quite noticeable. The difference in volume at the boiling point between *n*-alkanes and isomeric 2 : 2 : 3-trimethylalkanes is approximately twice as great as the difference between *n*-alkanes and isomeric trimethylalkanes in which all three methyl groups are in penultimate positions (2 : 2 : 2′-trimethylalkanes). Furthermore, the latter type of trimethyl-substitution does not cause as great a diminution in volume as do many types of dimethyl substitutions, whilst the 2 : 2 : 3-trimethylalkanes have smaller molal volumes than any other type here mentioned.

In Table XVIII are arranged several homologous series of alkanes in order of decreasing size of isomers,* summarizing the differences at the boiling point and at 20°.

The difference in order of the alkane series at the boiling point and at 20° is due chiefly not to difference in temperature coefficients of the densities, but to differences in the boiling points between *n*-alkanes and branched-chain alkanes. Since the boiling points of all branched alkanes are lower than the corresponding isomeric *n*-alkanes, the increase in molal

* The arrangement at 20° is based on the plot constructed by Calingaert and Hladky, reference 2.

volume between 20° and the boiling points for the branched chains is not as great as for the straight chains.

TABLE XVIII.

	At 20°.
Normal	2 : 2 : 2′-Me_3-
2-Me-	2 : 2′-Me_2-
3-Me-	2 : 2-Me_2-
2 : 2-Me_2-	2-Me-
2 : 2′-Me_2-	Normal
3 : 3-Me_2-	3-Me-
2 : 2 : 2′-Me_3-	3 : 3-Me_2-

The molal volumes of 1-alkenes at the boiling points are less than those of *n*-alkanes with the same number of carbon atoms. The 1-alkynes have still smaller molal volumes at the boiling point. These relationships among the three series also are true at 20°, and may be explained by the loss of hydrogen atoms as unsaturation increases, thus leaving smaller molecules.

While at 20° the density of members of any homologous series of aliphatic hydrocarbons increases regularly with the molecular weight, this relationship appears not to be true at the boiling point. Thus for *n*-alkanes at the boiling point, the density for the first few members increases rapidly, then between hexane and heptane goes through a maximum, and for the remainder of the series decreases slowly. The branched alkanes, the 1-alkenes, and the 1-alkynes show similar maxima (see Table XIX and Fig. 1). It is possible, however, that these maxima for certain series are only the results of the extrapolations, since small changes in temperature coefficients of the densities might alter the form of the density *v.* number of carbon atoms curves in cases where large extrapolations have been made.

TABLE XIX.

Density at the Boiling Point.

n.	*n*-Alkanes.		1-Alkenes.		1-Alkynes.	
	Obs.*	Calc.	Obs.	Calc.	Obs.	Calc.
1	0·4289	0·4240	—	—	—	—
2	0·5356	0·5464	0·5676	0·5651	0·6213	0·6253
3	0·5813	0·5818	0·6104	0·6099	0·6714	0·6668
4	0·6025	0·6017	0·6255	0·6277	—	0·6788
5	0·6121	0·6110	0·6321	0·6332	0·6718	0·6786
6	0·6155	0·6152	0·6339	0·6327	0·6700	0·6728
7	0·6152	0·6143	—	—	0·6636	0·6644
8	0·6129	0·6120	—	—	0·6565	0·6546
9	0·6093	0·6095	—	—	—	—
10	0·6049	0·6058	—	—	—	—

* At the boiling points obtained from equation (1); boiling point densities of all other hydrocarbons are at the boiling points given by Egloff, reference 4.

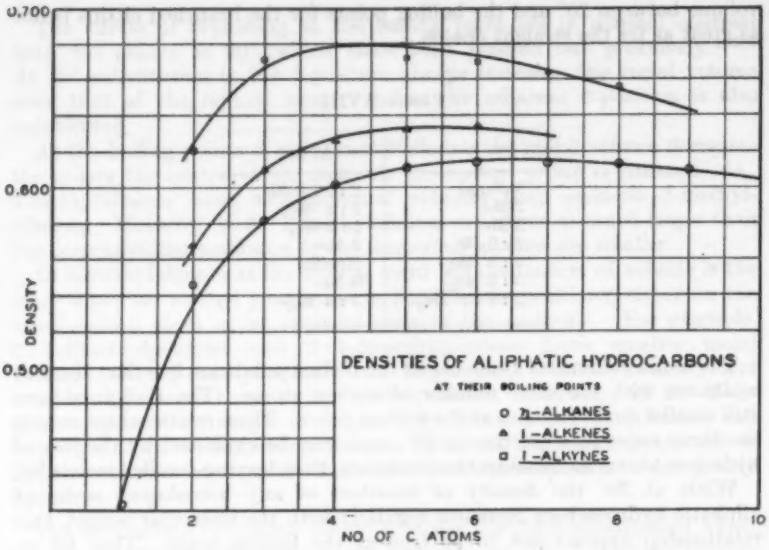


FIG. 1.

PART II. MOLAL VOLUME-BOILING POINT RELATIONSHIPS.

Little work has been done previously on the correlation of the boiling point molal volumes with the boiling points. Schuster,[8] in 1926, proposed an equation for *n*-alkanes, but the fit is not very good:

$$\log V = 1{\cdot}3612 + 0{\cdot}002287\ T.$$

By combining equations (1) and (3) of Part I, a new equation, (4), is obtained:

$$\log (V - k) = \frac{c}{a'} T + \log a - \frac{k'}{a'} c \quad . \quad . \quad . \quad (4)$$

Equation (4) may be reduced to the simple form:

$$\log (V - k) = AT + B, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which V is the molal volume at the boiling point; T is the boiling point temperature on the absolute scale, and k, A, and B are constants. The value of k is the same as in equation (2), and the other constants are related thus:

$$A = \frac{c}{a'}; \quad B = \log a - k'A$$

If the substitution $T = t + 273{\cdot}16°$ is made, where t is the boiling point on the Centigrade scale, a more convenient equation, (6), is obtained:

$$\log (V - k) = At + B' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which $B' = B + 273{\cdot}16\ A = \log a - A(k' - 273{\cdot}16)$.

Since in equation (1) only k' varies from series to series, in equation (6) A will change only with the degree of unsaturation, and B' will change for each series, whilst k remains constant for all series.

The values of A and B' were calculated for all homologous series to which both equations (1) and (2) apply. Since equation (1) does not hold for the initial members of some of the series, equation (6) is likewise not applicable to these members—namely, methane, 2-methylpropane, 2 : 2-dimethylpropane, ethene, ethyne, propyne, and butyne-1.

Equation (6) does not reproduce the experimental molal volume data quite as accurately as does equation (2), since there are small errors in the variable t, whereas there are none in the variable n. The mean deviation

TABLE XX.

n-*Alkanes*.

$k' = -416{\cdot}31$, $a' = 745{\cdot}42$.

$\log (V + 37{\cdot}00) = 0{\cdot}00177408t + 2{\cdot}12622$.

n.	t.	V obs.	V calc.	ΔV
2	−88·5	55·03	56·16	1·13
3	−42·2	75·80	75·55	−0·25
4	− 0·5	96·59	96·45	−0·14
5	36·08	118·09	117·96	−0·13
6	68·8	140·07	140·12	0·05
7	98·4	163·10	162·89	−0·21
8	125·6	186·64	186·33	−0·31
9	150·71	210·42	210·51	0·09
10	174·04	234·86	235·26	0·40

TABLE XXI.

2-*Methylalkanes*.

$k' = -424{\cdot}51$.

$\log (V + 37{\cdot}00) = 0{\cdot}00177408t + 2{\cdot}13926$.

n.	t.	V obs.	V calc.	ΔV.
5	27·95	117·81	117·47	−0·34
6	60·20	139·03	139·22	0·19
7	89·7	162·34	161·79	−0·55
8	117·2	185·88	185·42	−0·46
9	143·0	210·07	210·14	0·07
10	166·8	233·24	235·38	2·14

TABLE XXII.

3-*Methylalkanes*.

$k' = -422{\cdot}88$.

$\log (V + 37{\cdot}00) = 0{\cdot}00177408t + 2{\cdot}13237$.

n.	t.	V obs.	V calc.	ΔV.
6	63·2	137·90	138·59	0·69
7	91·8	159·91	160·35	0·44
8	119	183·99	183·54	−0·45
9	144·18	207·46	207·43	−0·03
10	167·8	231·53	232·19	0·66

of the calculated from the observed molal volumes for thirty-five alkanes is 0·61 ml./mol, and for all forty-three aliphatic hydrocarbons considered, 0·62 ml./mol. The agreement of the individual hydrocarbon values is shown in Tables XX to XXVIII and summarized in Table XXIX.

TABLE XXIII.

3-Ethylalkanes.

$k' = -423{\cdot}01.$

$\log (V + 37{\cdot}00) = 0{\cdot}00177408t + 2{\cdot}12914.$

n.	*t.*	*V* obs.	*V* calc.	ΔV.
7	93·3	158·64	160·09	1·45
8	118·9	182·06	181·82	−0·24
9	143·1	205·30	204·55	−0·75

TABLE XXIV.

2 : 2-Dimethylalkanes.

$k' = -435{\cdot}34$

$\log (V + 37{\cdot}00) = 0{\cdot}00177408t + 2{\cdot}15505.$

n.	*t.*	*V* obs.	*V* calc.	ΔV.
6	49·7	138·41	138·08	−0·33
7	78·9	161·14	160·25	−0·89
8	107·0	183·85	184·25	0·40
9	130·4	207·02	206·44	−0·58

TABLE XXV.

2 : 3-Dimethylalkanes.

$k' = -425{\cdot}88.$

$\log (V + 37{\cdot}00) = 0{\cdot}00177408t + 2{\cdot}13423.$

n.	*t.*	*V* obs.	*V* calc.	ΔV.
6	58·0	137·30	135·64	−1·66
7	89·7	158·32	159·50	1·18
8	115·7	181·19	181·52	0·33
9	140·6	205·59	204·92	−0·67

TABLE XXVI.

3 : 3-Dimethylalkanes.

$k' = -430{\cdot}10.$

$\log (V + 37{\cdot}00) = 0{\cdot}00177408t + 2{\cdot}13870.$

n.	*t.*	*V* obs.	*V* calc.	ΔV.
7	86·0	157·79	158·55	0·76
8	111	180·82	179·56	−1·26
9	137·2	203·22	204·04	0·82
10	161·2	227·42	228·88	1·46

TABLE XXVII.

1-Alkenes.

$k' = -421{\cdot}91$

$\log (V + 37{\cdot}00) = 0{\cdot}00186279t + 2{\cdot}11304.$

n.	t.	V obs.	V calc.	ΔV.
3	−47·7	68·93	68·73	−0·20
4	− 6·47	89·69	89·18	−0·51
5	30·1	110·95	110·61	−0·34
6	63·5	132·76	133·35	0·59

TABLE XXVIII.

1-Alkynes.

$k' = -413{\cdot}81.$

$\log (V + 37{\cdot}00) = 0{\cdot}00194684t + 2{\cdot}06310.$

n.	t.	V obs.	V calc.	ΔV.
5	39·7	101·39	101·16	−0·23
6	70·9	122·73	121·90	−0·83
7	99·6	144·92	143·72	−1·20
8	126·0	167·85	166·42	−1·43

TABLE XXIX.

Values of A and B′ for Aliphatic Hydrocarbons.

Series.	$A \times 10^3$.	B'.	Mean deviation.
n-Alkanes	1·77408	2·12622	0·30
2-Methylalkanes	,,	2·13926	0·62
3-Methylalkanes	,,	2·13237	0·45
3-Ethylalkanes	,,	2·12914	0·81
2 : 2-Dimethylalkanes	,,	2·15505	0·55
2 : 3-Dimethylalkanes	,,	2·13423	0·96
3 : 3-Dimethylalkanes	,,	2·13870	1·08
1-Alkenes	1·81827	2·11304	0·41
1-Alkynes	1·94684	2·06310	0·92

SUMMARY.

By means of equations of the type

$$V = a(n + 4{\cdot}4)^c + k$$

the molal volumes of sixty-three aliphatic hydrocarbons (arranged in fourteen different homologous series) at their boiling points have been correlated with the number of carbon atoms in the molecule. The mean deviation of the calculated from observed values is 0·39 ml./mol.

By means of equations of the type

$$\log (V - k) = At + B'$$

the boiling-point molal volumes of forty-three aliphatic hydrocarbons in nine homologous series have been correlated with the boiling points, with a mean deviation of 0·62 ml./mol.

The effect of the structure of the hydrocarbon molecule on the molal volume at the boiling point is discussed, and comparisons are made with the effect at 20°.

References.

[1] Boord, C. E.: "The Science of Petroleum" (London: Oxford University Press, 1938), Vol. II, p. 1349.
[2] Calingaert, G., and Hladky, J. W.: *J. Amer. chem. Soc.*, 1936, **58**, 153.
[3] Edgar, G., and Calingaert, G.: *ibid.*, 1929, **51**, 1540.
[4] Egloff, G.: "Physical Constants of Hydrocarbons" (New York: Reinhold Publishing Corp., 1939), Vol. 1.
[5] Egloff, G., Sherman, J., and Dull, R. B.: *J. phys. Chem.*, 1940, **44**, 730.
[6] Kopp, H.: *Annalen*, 1842, **41**, 79; 1855, **96**, 153, 303.
[7] Le Bas, G.: "The Molecular Volumes of Liquid Chemical Compounds" (London: Longmans, Green and Co., 1915), p. 140.
[8] Schuster, F.: *Z. Elektrochem.*, 1926, **32**, 550.

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ON THE RATE OF REACTION IN THE SYSTEM MINERAL OIL-OXYGEN. A CONTRIBUTION TO THE KNOWLEDGE OF OIL STABILITY.*

By D. J. W. Kreulen, F.Inst.Pet., and D.Th. J. ter Horst.

PART I.—GENERAL INTRODUCTION.

This series of papers represents a study of the reaction velocities in the system mineral oil-oxygen. Previous investigations have shown that there appears to exist a certain relation between oil properties and molecular structure. Further scientific work is needed to emphasize this relation and to investigate its nature. In this connection it is pointed out that many experiments mentioned in the literature would have been more complete and of greater general importance if the average structure of the oil molecule had been given. This omission is the more regrettable since Waterman and co-workers [1] have shown how particulars of the average constitution of the oil molecule can be obtained from a few easily determined constants. By this method the average constitution of the oil molecule can be given in percentages of aromatic rings, naphthenic rings, paraffinic side-chains, and average number of rings per molecule. Moreover, the branching of the paraffinic side-chains is established as the number of extra tertiary carbon atoms above those which agree logically with the most simple way of coupling the components to the molecule. In this statement the figure for the average number of rings per molecule is accurate if the average molecular weight is taken into account.

In order to calculate the percentages of naphthenic rings and paraffinic side-chains, a supposition is made—namely, that polycyclic 6-ring naphthenes are under consideration.

It would have been logical to have started our experiments with 100 per cent. paraffins. We did not do so for the simple reason that it is difficult to determine the constants for the higher members of the paraffinic series, as they have high melting points. Moreover, paraffins as regards their properties are so far removed from lubricating oils that we had no immediate interest in them. We chose, therefore, as the first oil, a medicinal paraffin oil, which may be considered to be a lubricating oil completely saturated with hydrogen.

This oil had the following constants: molecular weight 445; density $\frac{20}{4} = 0{\cdot}8833$; refractive index $D_{20} = 1{\cdot}4828$; critical solution temperature (aniline point) = 109·0° C.; surface tension at 20° C. = 32·1 dyne per cm.; and specific dispersion $\frac{(N_{C'} - N_C)10^4}{d} = 158$. From these constants we derive the following figures for the "ring analysis": Aromatic rings 0 per cent.; naphthenic rings 37 per cent.; paraffinic side-chains 63 per cent.; extra tertiary carbon atoms = 5 (which corresponds to a very

* Paper received 5th March, 1940.

moderate branching of the paraffinic side-chains); and average number of rings per molecule = 2·8.

Two methods are available for the measurement of the rate of reaction in the system liquid–gas.

A. Method Based on the Principle of A. Titoff.[2]

This method is characterized by the application of a pure homogeneous medium. The gas, in this case oxygen, is dissolved in the liquid. The liquid phase is then completely separated from the gas phase and allowed to react at the desired temperature. During the reaction, samples are drawn off, and the quantity of gas still present in them is determined. It is possible to calculate the velocity K of the reaction from the alteration of the gas concentration, according to the equation $K = \frac{1}{t}, lg \frac{A}{(A-x)}$, A being the quantity of gas in gram molecules per litre at the beginning of the experiment and $(A - x)$ that at the time t. As the active mass of the liquid remains practically constant, the monomolecular law is followed.

In our case this method has a disadvantage, due to the slight solubility of oxygen in oil. The problem is thus to estimate relative small quantities of dissolved oxygen with sufficient accuracy, which is somewhat difficult.

The method was applied to oils by Ornstein and co-workers.[3]

B. Method According to R. Luther and J. Plotnikow.[4]

In this method also the liquid phase as well as the gas phase is present during the reaction. The gas phase is continually stirred into the liquid phase. Both form together one closed system, precautions being taken to prevent any escape of gas. Thus, at the end of the experiment the total oxidation products which are formed are obtained.

In such an experiment the relation between reaction velocity and supply velocity of the oxygen is of primary importance. The method and velocity of stirring are critical, and for this reason the method and apparatus of Luther and Plotnikow, as modified by W. Reinders and S. I. Vles,[5] was used.

Our apparatus is shown in Fig. 1.

A hollow stirrer of special construction is used. The lower part, which has the form of a Segner's water-wheel, serves to disperse the gas into the liquid. At the top of the stirrer a couple of small openings are made, through which the gas is allowed to enter. A glass partition placed in the liquid prevents too much whirling, so that the division of the gas is increased. The division of the gas becomes more intensive with increased stirring velocity. Reaction velocities are measured only if the liquid remains continually saturated. It is therefore necessary to choose that stirring velocity at which this requirement is fulfilled. In our case we applied a stirring velocity of 1500 revs. per minute. This stirring velocity will be justified below.

In order to be sure of a constant pressure of oxygen, the experiments in this apparatus were carried out under a slight constant pressure (5 cm. Hg).

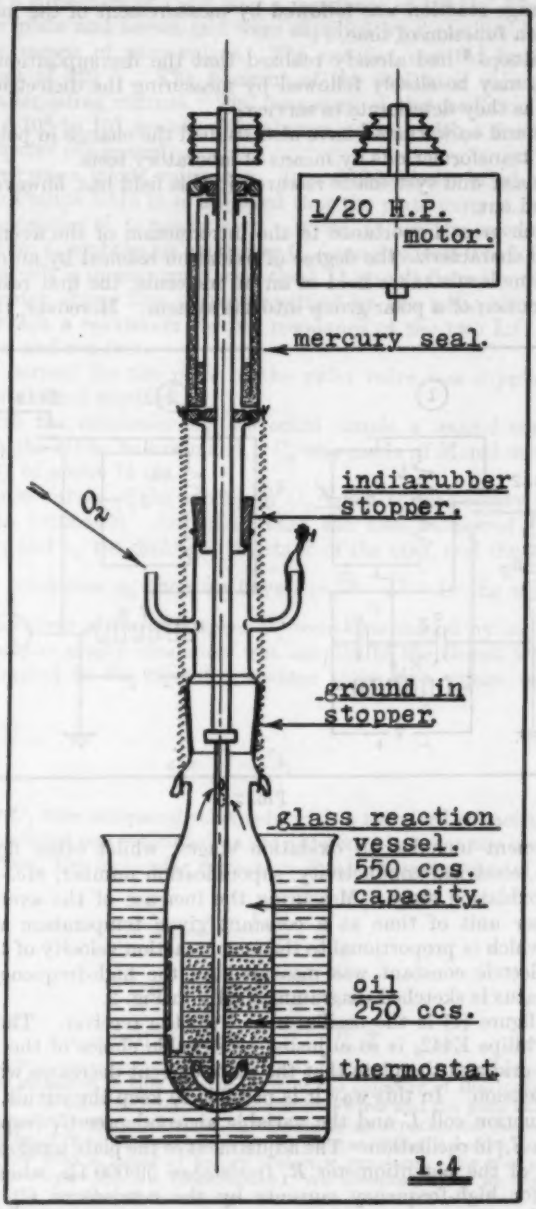

1/20 H.P.
motor.
mercury seal.
indiarubber
stopper.
O_2
ground in
stopper.
glass reaction
vessel.
550 ccs.
capacity.
oil
250 ccs.
thermostat.
1:4

FIG. 1.

The average reaction was followed by measurement of the mean dipole moment as a function of time.

W. N. Stoops [6] had already realized that the decomposition of transformer oils may be closely followed by measuring the dielectric constant of the oils as they deteriorate in service.

Ornstein and co-workers [7] have also studied the change in polar characteristics of transformer oils by means of laboratory tests.

An extensive and systematic research in this field has, however, not yet been carried out.

We attach great importance to the introduction of the average dipole moment to characterize the degree of oxidation reached by an oil, since if an oxygen molecule takes hold of an oil molecule, the first result will be the introduction of a polar group into the system. Moreover, the average

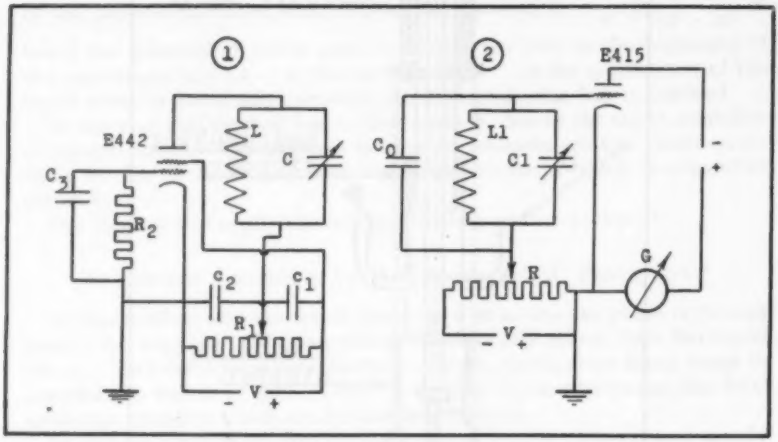


FIG. 2.

dipole moment includes all oxidation stages, whilst other figures—*e.g.*, acid value, electrical conductivity, saponification number, etc.—represent only the oxidation stage. Measuring the increase of the average dipole moment per unit of time at a constant given temperature will give a quantity which is proportional to the mean reaction velocity of the system.

The dielectric constant was measured by the high-frequency method. The apparatus is sketched diagrammatically in Fig. 2.

In this figure (1) is the oscillator and (2) the receiver. The oscillator valve, a Philips E442, is so adjusted by suitable choice of the tension on the screen-grid and the plate that the plate current decreases with increasing plate tension. In this way it is possible to keep the circuit, consisting of the induction coil L and the variable air-condenser C_1 (capacity from 0 to 500 $\mu\mu$ F.) in oscillation. The adjustment of the plate tension is possible by means of the potentiometer R_1 (resistance 50·000 Ω), which is short-circuited for high-frequency currents by the condensers C_1 and C_2 of 2 μ F. each. The control grid of the valve was connected to the cathode

by means of a condenser of 1 μ F. and a resistance of 10^6 Ω. The voltage necessary for plate and screen-grid were supplied by a rectifier which was stabilized by means of neon-valves. The rectifier was fed by an alternating tension of 220 V. The filament of the oscillator valve was fed directly by alternating current. The frequency of the oscillator could be varied from $3 \cdot 10^5$ to 10^6 cycles. We always worked with a frequency of about $3 \cdot 10^5$ cycles per second.

The receiver was a triode voltmeter. By suitable choice of grid-tension, a radio valve Philips E415 is so adjusted that the plate current, measured by the galvanometer G, is nearly zero. If we adjust the circuit formed by the induction L_1 and the air condenser C_1 (capacity from 0 to 500 μμ F.), so that this circuit is in resonance with the L.C. circuit from the oscillator, the galvanometer shows this current rectified by the radio valve. This current will reach a maximum for full resonance of the two L.C. circuits from oscillator and receiver.

The direct current for the plate of the radio valve was supplied by a second neon stabilized rectifier.

Parallel with the condenser C_1, we could couple a second condenser, C_0, filled with the oil to be examined. C_0 was made of Monel metal, and had a capacity of about 74 cm.

The resonance values of the condenser C_1, when C_0 was empty or filled with oil, were estimated. Assuming that the two values of C_1 were respectively c_1 and c_2, the dielectric constant of the oil ε, and the capacity of the empty condenser c_0, then we have $\varepsilon = \dfrac{c_2 - c_1}{c_0}$. In the same way the resonance values of the condenser C_1 were determined by us, for the condition when the empty condenser was coupled to the circuit and when it was not coupled to the circuit. Assume these two values to be c_2' and c_1'.*

Now we have:

$$\varepsilon = \frac{c_2 - c_1}{c_2' - c_1'}.$$

The condenser C_1 was compared relatively with a standard capacity.

The dipole moment was estimated as the difference between the molecular polarization P and the molecular refraction P_0 at a temperature of 20° C.

Here

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d}$$

$$P_0 = \frac{N^2 - 1}{N^2 + 2} \frac{M}{d}$$

$$\bar{\mu} = 0{\cdot}0127 \,.\, 10^{-18} \sqrt{(P - P_0)T}$$

* The capacity measured in this way is not only the capacity of that part of the condenser which can be filled with oil. The connection wires and the glass insulation of the condenser itself exert their influence. Therefore in our experiments this capacity c_0 was calculated back from measurements which were carried out before and after filling the condenser with a liquid of known dielectric constant. For this purpose we used molecular-weight benzene (Kahlbaum). We accepted 2·285 as being the most probable value for the dielectric constant $\varepsilon_{20°}$. The data obtained by our experiments may be considered to be reliable to within $\frac{1}{2}$ per cent.

where ε = dielectric constant, M = molecular weight, d = density, N = refractive index, $\bar{\mu}$ = mean dipole moment, and T = absolute temperature.

The factor $0{\cdot}0127 \cdot 10^{-18}$ is the numerical value for $\sqrt{\frac{9K}{4\pi N}}$, where K represents the Boltzmann constant and N the number of Avogadro. A series of observations with our oil is given in Table I. The oxidation was affected at 100° C. During the experiment a spider of electrolytic copper was attached to the stirrer. Its surface amounted to 25 cm.^{2}. A stirring velocity of 1500 revs. per minute was applied. The molecular weight was determined by the cryoscopic method using naphthaline as a solvent.*

TABLE I.

Time, hrs.	Density, 20°.	Refractive index, $D_{20°}$.	$\varepsilon_{20°}$.	Mol. weight.	Mol. refraction. Observed.	Mol. refraction. Corrected.	Mol. polarization.	Mol. polarization minus mol. refraction.	$\bar{\mu} \cdot 10^{18}$ e.s.u.	Dispersion $(N_F - N_C)10^5$.	Specific dispersion $\frac{N_F - N_C}{d} \cdot 10^4$.
0	0·8833	1·4828	2·193	445	143·82	143·21	143·33	0	0	139	158
6½	0·8833	1·4828	2·192	445	143·82	143·21	143·28	0	0	139	158
13½	0·8833	1·4828	2·190	445	143·82	143·21	143·08	0	0	139	158
20½	0·8833	1·4828	2·190	445	143·82	143·21	143·08	0	0	139	158
27½	0·8833	1·4828	2·193	445	143·82	143·21	143·33	0	0	139	158
33	0·8833	1·4828	2·191	445	143·82	143·21	143·18	0	0	139	158
40	0·8832	1·4829	2·199	445	143·86	143·25	143·89	0·64	0·17	139	158
47	0·8844	1·4829	2·225	445	143·69	143·08	145·87	2·79	0·36	139	157
52	0·8860	1·4831	2·241	445	143·47	142·86	146·96	4·10	0·44	139	157
57	0·8878	1·4832	2·279	445	143·20	143·59	149·82	7·23	0·58	139	157
62	0·8898	1·4833	2·314	445	142·89	142·28	152·33	10·05	0·69	139	156
67	0·8926	1·4839	2·379	445	142·62	142·01	156·99	14·98	0·84	139	156
72	0·8961	1·4839	2·457	445	142·04	141·43	162·34	20·91	0·99	139	155
77	0·8997	1·4842	2·536	445	141·55	140·94	167·47	26·53	1·12	139	155

143·21

In connection with the dipole moment the question arose whether an orientation of the polar molecules had taken place. This, however, appeared not to be the case.*

During the oxidation the specific dispersion remained practically constant. In each case no increase was noted. Thus cyclization certainly did not occur during our experiments.

In Fig. 3 the increase of the average dipole moment is plotted as a function of time.

From this figure it is apparent that no appreciable increase of polar compounds can be observed until an induction period, with an initial period of very slow reaction, is passed. Beyond this induction period there exists a linear relation between $\bar{\mu}$ and the time of oxidation. During our experiments we got the impression that the introduction of polar compounds into the system did not begin suddenly, but that a slight and increasing reaction exists in the latter part of the induction period.

* To control this the dipole moment of the oil, after an oxidation for 77 hours, was estimated by means of the dilution method (P. Debye, "Polare Molekeln," Leipzig, 1929). As dilution solvent we used benzene. With the dilution method an average dipole moment of $1{\cdot}17 \times 10^{-18}$ e.s.u. was found, which is in good agreement with the figure $1{\cdot}12 \times 10^{-18}$ e.s.u. stated for the non-diluted oil.

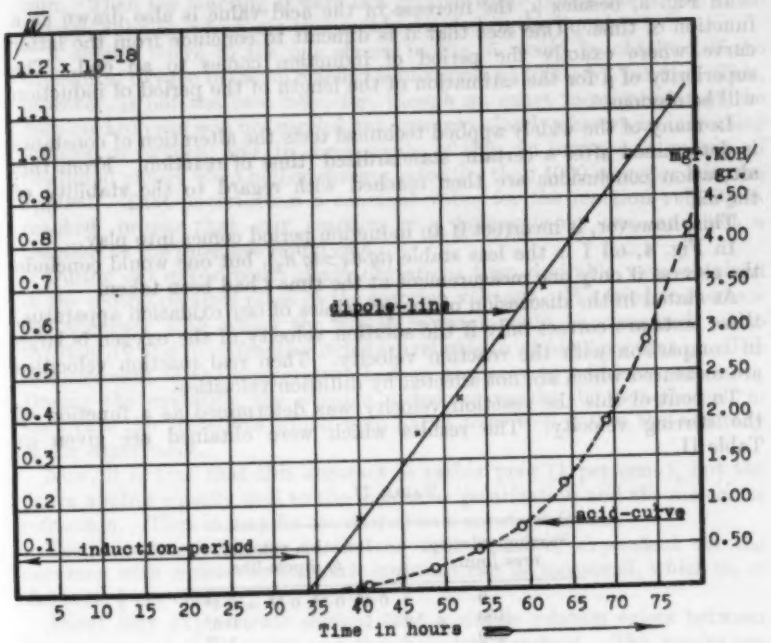

$\sqrt{w}$
1.2 x 10^{-18}
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
mgr.KOH/gr.
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
dipole-line
acid-curve
induction-period
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
Time in hours

FIG. 3.

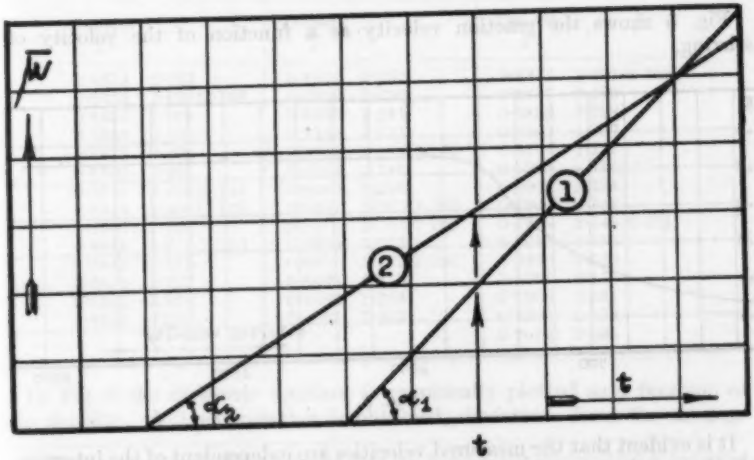

$\sqrt{w}$
1
2
α_2
α_1
t
t

FIG. 4.

In Fig. 3, besides $\bar{\mu}$, the increase of the acid value is also drawn as a function of time. One sees that it is difficult to conclude from the latter curve where exactly the period of induction comes to an end. The superiority of $\bar{\mu}$ for the estimation of the length of the period of induction will be obvious.

In many of the widely applied technical tests the alteration of constants is determined after a certain, standardized time of reaction. From this alteration conclusions are then reached with regard to the stability of the oil.

This, however, is incorrect if an induction period comes into play.

In Fig. 4, oil 1 is the less stable ($tg\ d_1 > tg\ d_2$), but one would conclude the reverse if only one measurement at the time t had been taken.

As stated in the discussion of the principles of our oxidation apparatus, these tests are correct only if the solution velocity of the oxygen is large in comparison with the reaction velocity. Then real reaction velocities are measured which are not affected by diffusion velocities.

To control this the reaction velocity was determined as a function of the stirring velocity. The results which were obtained are given in Table II.

TABLE II.

Stirring velocity, revs./min.	Reaction velocity, *tg* dipole-line.
0	$0{\cdot}4^0$, $0{\cdot}5^0$, $0{\cdot}3^3 = 0{\cdot}4^4$
450	$0{\cdot}6^5$
950	$1{\cdot}3^9$
1500	$1{\cdot}3^9$
2000	$1{\cdot}2^6$

Fig. 5 shows the reaction velocity as a function of the velocity of stirring.

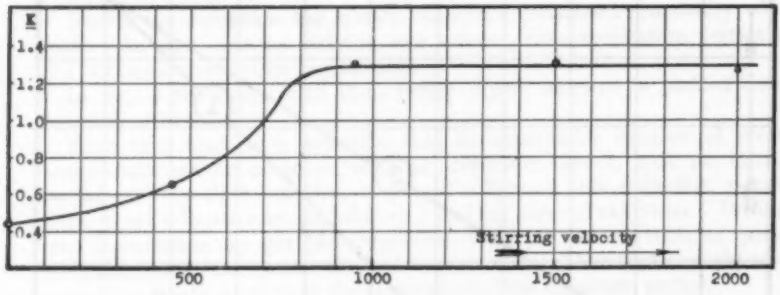


FIG. 5.

It is evident that the measured velocities are independent of the intensity of stirring when the latter is higher than 1000 revs. per min. To be on the safe side our experiments were made at a stirring velocity of 1500 revs. per

min. Then the reacting system is a greyish-white liquid due to the small oxygen bubbles, which are thoroughly divided in the liquid.*

A similar curve to the one shown in Fig. 5 would be obtained if the division of oxygen in the oil reached a maximum at 1000 revs. per min. This, however, is not the case here, for, though an exact measurement of the dispersed oxygen was not carried out, one may clearly observe an increasing division of oxygen, and, in consequence of this, an increase in volume of the liquid phase, when higher stirring velocities than 1000 revs. per min. are applied. That nevertheless a constant value for the reaction velocity is reached proves that our reaction is a homogeneous one, and not a reaction at the interface liquid–gas.

During our experiments larger deviations than desirable were obtained in the second decimal place of the reaction velocity. We tried to increase the accuracy with which the dipole moment could be measured. Also the density and the refractive index are reliable to within 2 per cent.$_{00}$. The measurement of the temperature had an accuracy to within 1 per cent.$_0$. During the oxidation the average molecular weight did not change, in each case the variations which were found were well within the accuracy of the experiment.

Now, it is true that this accuracy is rather poor ($\frac{1}{2}$ per cent.), but the figure applies equally well to the molecular polarization and the molecular refraction. Thus it may be considered as a constant factor.

The experimental error is, in the first instance, dependent on the accuracy with which the dielectric constant can be measured, which is, at the best, $\frac{1}{2}$ per cent.

About fifty experiments showed that a simple relation exists between the increase of the density and the dielectric constant. The results are collected in Table III.

TABLE III.

Density d_4^{20}.		Density d_4^{20}.		Density d_4^{20}.	
0·8833	2·193	0·8855	2·233	0·8885	2·291/2·308
0·8834	2·194/2·196	0·8856	2·232	0·8887	2·299
0·8835	2·198	0·8860	2·241	0·8888	2·298
0·8838	2·200	0·8862	2·251	0·8892	2·307
0·8839	2·207	0·8863	2·244/2·246	0·8894	2·312
0·8840	2·201	0·8864	2·246	0·8898	2·314
0·8841	2·208/2·210	0·8866	2·245	0·8900	2·324
0·8844	2·204/2·225	0·8867	2·262/2·263	0·8904	2·344
0·8847	2·221	0·8872	2·264/2·267	0·8908	2·340/2·354
0·8848	2·212/2·223	0·8873	2·273	0·8915	2·356
0·8849	2·229	0·8878	2·279/2·291	0·8920	2·380
0·8851	2·227	0·8880	2·275	0·8961	2·457
0·8852	2·228	0·8882	2·284	0·8968	2·461
0·8853	2·233	0·8883	2·305	0·8997	2·536
				0·9019	2·594

In Fig. 6 the dielectric constant is graphically plotted as a function of the density. A linear relation is obtained, deviations from the average

* The stated critical stirring velocity does not increase our appreciation of technical tests in which quantities varying from 2 to 15 litres per hour are introduced into the oil.

line lying well within the accuracy of the experiment. Consequently it is possible to increase the accuracy with which the average dipole moment is estimated by the following procedure.

The dielectric constant which is found is used to check whether the relationship between density and dielectric constant holds. This being the case, the average dipole moment is calculated with that value of the dielectric constant which is obtained from the more exact density with the aid of Fig. 6.*

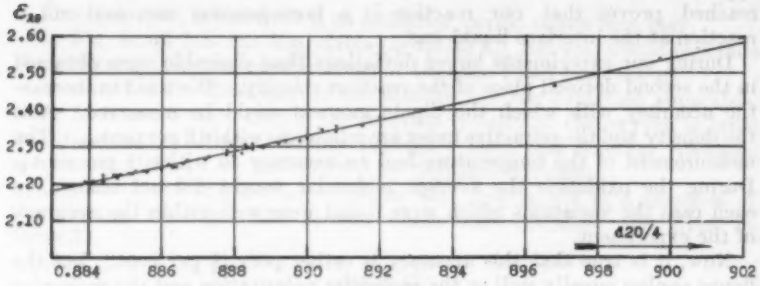


FIG. 6.

It is possible to explain this linear reaction between dielectric constant and density in the following way. The general scheme of reaction is given by:

a molecules oil + b molecules oxygen $\longrightarrow$ c molecules polar oil + d molecules water.

We can easily show that the increase of density $\Delta\rho$ is given by

$$\Delta\rho = x\frac{b}{a}m_{O_2},$$

where x is the number of oil molecules oxidized and m_{O_2} the mass of an oxygen molecule.

The increase of the polarization per unit volume is given by:

$$\frac{\Delta\varepsilon}{\varepsilon_0 + 2} = \frac{4n}{3} \times \left(\frac{c}{a}A_p + \frac{d}{a}A_w - A_0\right)$$

where $\Delta\varepsilon$ = the increase of the dielectric constant, ε_0 = the dielectric constant of the unaltered oil, and A_0, A_p, and A_w = the polarization per molecule of the oil, polar oil, and water respectively.

* Further research is necessary to investigate if the same relation may be accepted for oils which contain aromatic rings (ordinary lubricating and transformer oils) respectively if the tangent of the straight line drawn in Fig. 6 is a function of molecular weight. This being known, the procedure becomes very simple, as the measurement of the dipole moment may then be substituted by a determination of density.

From these two relations we see that $\frac{\Delta\varepsilon}{\Delta\rho}$ is in first approximation a constant. If we substitute the values for ε_0 and m_{0_2}, we find:

$$\frac{\Delta\varepsilon}{\Delta\rho} = 0{\cdot}46 \,.\, 10^{24}\left(\frac{d}{a}A_w + \frac{c}{a}A_p - A_0\right).$$

J. W. Williams [9] measured the value for A_w, and from our measurements we can calculate A_0.

If we estimate $A_p \sim 2A_0$ (which is probably in connection with figures available in literature for the organic compounds in question), and if we introduce from Fig. 6, for $\frac{\Delta\varepsilon}{\Delta\rho} \sim 20{\cdot}77$ we find:

$$2a + 2b = 4c + 1d.$$

Now, in our case we study the oxidation of a molecule composed of naphthenic rings and paraffinic side-chains. That the first attack will take place at the paraffinic side-chain is very probable.

According to the literature, peroxides, aldehydes, ketones, acids, and water are also formed. If we give equal probabilities on the occurrence of the reactions:

oil + oxygen ⟶ peroxides + water
oil + oxygen ⟶ aldehydes + water
oil + oxygen ⟶ ketones + water
oil + oxygen ⟶ acids + water

we get an average:

$$7 \text{ oil} + 12 \text{ oxygen} \longrightarrow 9 \text{ polar compounds} + 5 \text{ water}$$

This is not so far from the scheme required by our function ε from ρ. If we had taken $A_p \sim 1\frac{1}{2}\, A_0$ we would find a similar result.*

As already stated, the increase on the average dipole moment $\bar{\mu}$ per unit of time at a given temperature is a quantity proportional to the mean reaction velocity. This quantity is in our experiments a constant value up to an average dipole moment of $0{\cdot}7$–$0{\cdot}8 \,.\, 10^{-18}$ e.s.u. is reached. This appears from Fig. 7.

In this figure we plotted the increase of the average dipole moment per unit of time as a function of the reciprocal value of the absolute temperature at which the experiments were carried out. A straight-line relation is found which confirms the results obtained by Ornstein and co-workers,[10] who studied the oxidation of transformer oils, using a method corresponding to that of Titoff.[11] From the slope of the straight line we compute an energy of activation of 21,300 calories per gram molecule.

If we continue the same experiments when the oil is oxidized further, we find the dotted line. Within a close range of the average dipole

* For the original oil we find $\epsilon = 2{\cdot}19$; $\frac{\epsilon - 1}{\epsilon + 2}\frac{1{\cdot}19}{4{\cdot}19} = 0{\cdot}285$.

For the polar compounds in which we are interested $\epsilon \sim 3$, thus $\frac{\epsilon - 1}{\epsilon + 2} \sim 0{\cdot}4$.

Therefore we choose $A_p \sim 1{\cdot}5/2\ A^0$.

moment $\bar{\mu}$ we obtain again a straight line (dotted line in Fig. 7). From the slope of this line we calculate an energy of activation of 27,600 calories per gram molecule.

We doubt the comparison of these two energies of activation, for if we connect in Fig. 7 the values found for subsequent dipole magnitudes, then it appears that each following value is somewhat higher than could be expected if the straight-line relation with foregoing measurements strictly hold.

It is quite possible that this phenomenon may be attributed to an increasing influence of the rupture of the molecule, resulting in the introduction of two polar compounds into the system instead of one. The

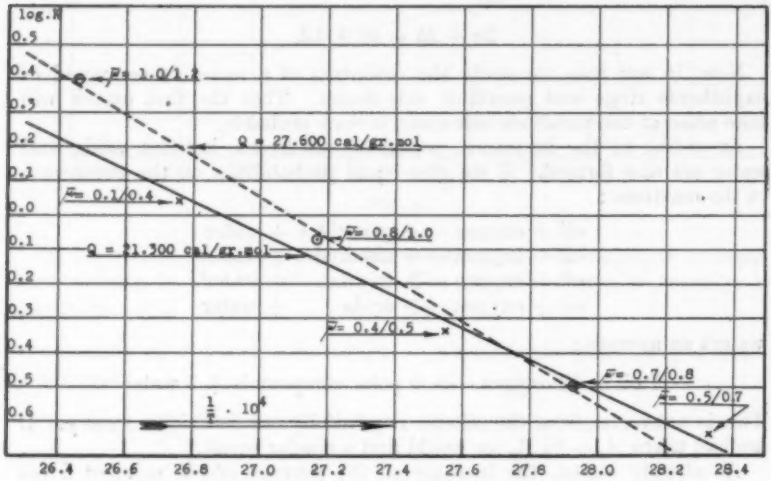


FIG. 7.

same alternative would explain why the acid value indicates relatively high figures for oxidation stages lying above the corresponding dipole moment of about 0·7 *D*. If we accept this hypothesis as true, it is evident that for the calculation of the energy of activation only these reaction velocities may come into account which are obtained at early oxidation stages of the oil.

The same phenomenon may be observed if, at a same temperature, the test is prolonged too long. Then, too, one may obtain figures which show a tendency to lie above the line found at the beginning of the test. Therefore it is of importance, if measurements of reaction velocity are realized by our method, to agree to which maximum stage of oxidation one wants to go. In our case we accepted as a limit 0·7–0·8 *D*. Only figures which are obtained beneath this limit were included in the straight-lined average relationship.

PART II.—THE INFLUENCE OF COPPER AND TIN.

We now go on to the influence of metals on the rate of reaction and on the length of the period of induction. This investigation is of importance as often, in literature, the catalytic action of certain metals (*e.g.* copper) is mentioned.

Our results, of course, are valid only for the oil which we investigated. However, data mentioned in the literature suggest that similar phenomena exert their influence during the oxidation of ordinary oils. The research will be extended to these oils.

In a first series of experiments copper filings (electrolytic copper) were used. These filings were passed through a sieve with 400 openings per sq. cm. The conditions of the test were: temperature 100° C.; stirring velocity 1500 revs. per min.; oxygen pressure 5 cm. Hg. Tests were

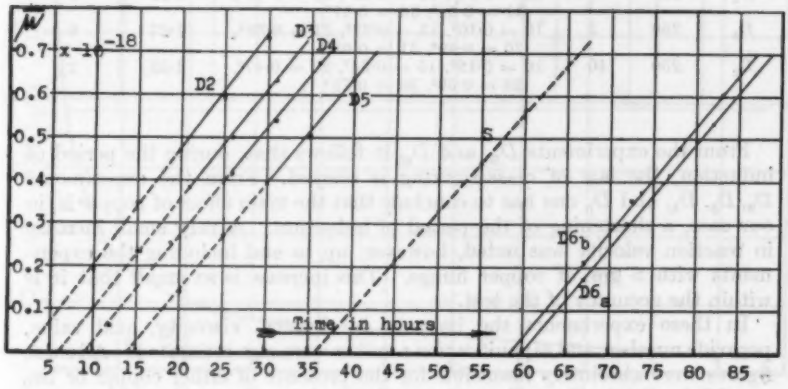


FIG. 8.

carried out without the addition of any metal, and subsequently with oils containing an increasing quantity of metal.

The progress of $\bar{\mu}$ was measured every five hours, and thus it was possible to deduce at the end of the experiment both the length of the induction period and the reaction velocity. The magnitude of the reacting surface of the filings is proportional to the number of grams which are added. After establishing the velocity of the reaction in the presence of metal (dotted lines in Fig. 8) the experiment was discontinued. The oil was then divided among four centrifuge tubes and centrifuged at a rate of 1500 revs. per min. The experiment was then continued with the supernatant oil, in which no solid metal was present. From this the lines drawn in Fig. 8 were obtained. The lines marked D_{6a} and D_{6b} refer to experiments with metal-free oil in different quantities (respectively 250 and 125 cm.^{3}). The lines marked D_2, D_3, D_4, and D_5 refer to experiments in which respectively 10, 5, $2\frac{1}{2}$, and $1\frac{1}{4}$ gm. of copper filings are added to 250 cm.^{3} of oil.

Line S refers to an experiment with tin which is mentioned below. The magnitude of the tin surface in this experiment is comparable with that of the copper surface in experiment D_4. The figures which were obtained are given in Table IV.

TABLE IV.

Test.	Cm.³ of oil.	Copper, gm.	Time = dipole moment (D).	Reaction velocity.	Induction period, hrs.
D_{6a}	250	0	67 = 0·17⁵, 72 = 0·31¹, 77 = 0·41⁵, 82 = 0·53⁴	1·21	60
D_{6b}	125	0	67 = 0·21⁵, 72½ = 0·35⁶, 78 = 0·47⁵, 83 = 0·60⁴	1·23	58½
D_5	250	1·25	20 = 0·14⁹, 25 = 0·27¹, 30 = 0·39³, 35 = 0·50⁵, 40 = 0·64	1·23	14
D_4	250	2·50	12 = 0·06⁸, 19 = 0·25⁴, 26 = 0·41⁶, 31 = 0·54⁰, 36 = 0·67⁷	1·25	9
D_3	250	5	10 = 0·10⁹, 15 = 0·23⁶, 21 = 0·38⁵, 26 = 0·49⁹, 31 = 0·63⁴	1·27	6
D_2	250	10	10 = 0·19⁵, 15 = 0·34⁷, 20 = 0·47⁶, 25 = 0·59³, 30 = 0·73¹	1·33	2½

From the experiments D_{6a} and D_{6b} it follows that, during the period of induction, the law of mass-working is obeyed. From the experiments D_2, D_3, D_4, and D_5 one has to conclude that the main effect of copper is, in our case, a shortening of the period of induction. A very small increase in reaction velocity was noted, however, up to and including the experiments with 5 gm. of copper filings. This increase is so small that it is within the accuracy of the test.

In these experiments the increase in density, viscosity, acid value, peroxide number, and saponification number were also estimated. All these figures were absolutely insensible for the presence of either copper or tin, provided one takes into account the length of the period of induction.

For an oxidation stage, corresponding with an average dipole moment of 0·5 D some constants are collected in Table V.

TABLE V.

Metal.	μ.	Acid value.	Saponification number.	Kinematic viscosity, 20° C.	Density $\frac{20}{4}$.
Tin	0·5 D	0·6	2·0	245 c.st.	0·8866
Copper	0·5 D	0·5	2·1	241 c.st.	0·8866
No metal . . .	0·5 D	0·5	2·0	243 c.st.	0·8866
Original oil . . .	—	—	—	216½ c.st.	0·8833

Neither copper nor tin, therefore, has any practical influence on the reaction velocity of the system. Only in the most extreme case may we expect even a small increase with copper—an increase, however, which can be neglected with respect to the primary effect resulting in a shortening

of the period of induction. In Fig. 9 the length of the period of induction is plotted as a function of the number of grams of copper filings which are added.

It appears that there is no straight-line relationship between the length of the induction period and the surface of copper which is added. The first quantities of the copper surface are the most active. This suggests the possibility of adsorption phenomena. To verify this suggestion the same quantity of copper filings (2½ gm.) was brought into contact with the oil for a different length of time. This contact was realized within the usual test-stirring conditions at 100° C. After the chosen length of time the experiment was discontinued. The copper filings were removed

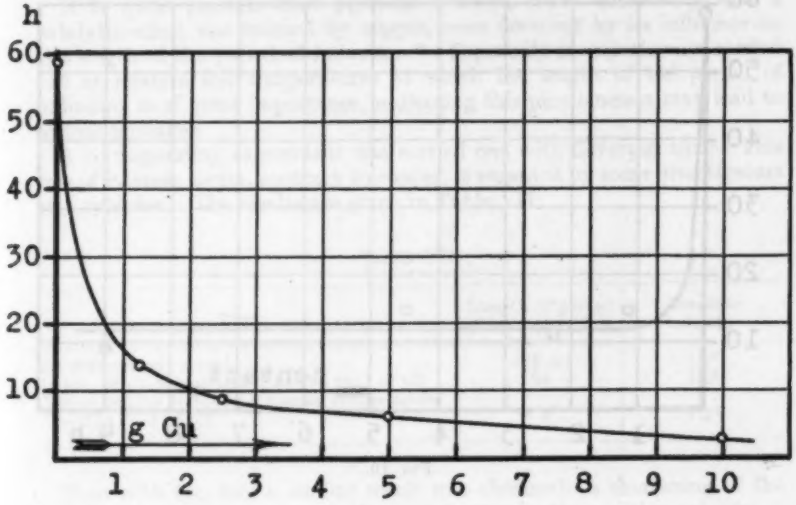


FIG. 9.

(by centrifuge) and the test was continued with the metal-free oil. The results obtained are given in Table VI.

TABLE VI.

Time of contact of 2½ gm. of copper filings and 250 cm.³ of oil, hrs.	Total length of the period of induction (time of contact included), hrs.
0	60–58½
9	9
4½	15½
2½	11
1½	15

In Fig. 10 the length of the induction period is graphically plotted as a function of the time of contact.

Thus it appears that the length of the period of induction is practically the same, either for a time of contact of, say, 1 hour, or for a time of contact corresponding with the complete length of the period of induction. Fig. 10 is a common curve of adsorption. To be absolutely sure, an experiment was carried out in which the contact of metal and oil was realized in a nitrogen atmosphere for 2 hrs. In this case, too, the induction period decreased from 60 hrs. for the original oil to 17 hrs. * for the metal-treated oil. This proves that we are justified in referring to the case as adsorption.

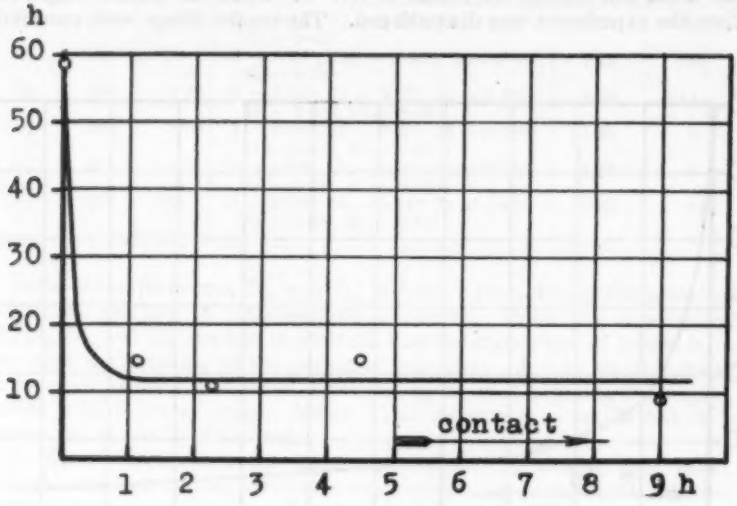


FIG. 10.

It seems very probable that certain compounds existing in the oil, which are able to delay or to prevent the oxidation for a certain length of time, are partly adsorbed by the copper surface.

If we accept the theory of C. Moureu and C. Dufraisse [12] † as correct, it

* In these 17 hrs. the time of contact is, of course, not included, as the oil was treated in a nitrogen atmosphere.

† The scheme of reaction, introduced by Moureu and Dufraisse is:

$$A + O_2 \longrightarrow A[O_2]$$

$$A[O_2] + B \longrightarrow A[O] + B[O]$$

acceleration: $B[O] + A \longrightarrow B + A[O]$, $A[O] \longrightarrow A \,.\, O$ (stable)

retardation or prevention: $B[O] + A[O] \longrightarrow A + B + O_2$

In this scheme B is the anti-oxidant and A the oxidizable compound. If O is placed between parentheses this means "not stable."

The objection against this theory is that $A(O_2)$ ought to meet quickly a B molecule as $A(O_2)$ may only be considered to be possible for a very short time.

However, anti-oxidants exert their influence even in extremely low concentrations. Then considerations about reaction velocities led to the conclusion that a $A(O_2)$ molecule will be surrounded by 40,000 molecules in a non-activated state. That is to say, that B is separated from the non-stable $A(O_2)$ molecule by a layer of, say,

is evident that—a metal surface being present—the length of the period of induction is a function of the time necessary to destroy that part of the anti-oxidant which is not absorbed.

The largest quantity of anti-oxidant is adsorbed by the first sq. cms. of metal surface (largest concentration of anti-oxidants). This explains why the first quantities of metal which are added exert such a great effect. The subsequent quantities of metal meet with lower concentrations of the anti-oxidant, thus the adsorption, and consequently its effect on the length of the period of induction, decreases.

After passing the induction period the metal is apparently completely inert; it is therefore entirely unjustified to speak about a catalytic effect in our case.

It is quite possible that previous workers, when concluding that a catalytic effect was exerted by copper, were deceived by its influence on the length of the period of induction.* Especially in experiments carried out at relative low temperatures at which the length of the period of induction is of great importance, neglecting this phenomenon may lead to serious mistakes.

A corresponding experiment was carried out with Chempur tin.† This was of interest, as tin, contrary to copper, is regarded by some investigators as a retarder. The results are given in Table VII.

TABLE VII.

Test.	Length of period of induction, hrs.	Reaction velocity.
Oil without any metal	58½–60	$1{\cdot}2^2$
2½ gm. of tin filings added to 250 cm.^{3} of oil .	36	$1{\cdot}2^6$
Corresponding surface of copper filings added to 250 cm.^{3} of oil	8	$1{\cdot}2^4$

Thus with tin, too, a similar result was obtained—a shortening of the period of induction and practically no influence on the reaction velocity.

Tin is evidently less active than copper with regard to the shortening of the induction period. As most of the anti-oxidants contain polarizable nitrogen containing groups,[13] these experiments affirm the well-known fact of a higher relative adsorption affinity for these compounds in the case of copper compared with that of tin.

Certain investigators supposed that the action of metals on oil would

20 molecules thick. In this case the collision change is rather small, and yet, to explain the phenomenon, it ought to be large. The aid hypothesis that the reaction will take place at the interface liquid–gas, which means a larger concentration, and, consequently, a larger collision change, is not acceptable according to our measurements.

It is possible that the assumption of reaction chains, which may be broken by anti-oxidants, will give a satisfactory explanation.

* Compare Fig. 4 in Part I of this paper.

† Composition according to Quin's "Metal Handbook and Statistics," 1939: Sn = 99·989 per cent.; Sb = 0·005 per cent.; As = nil; Pb = 0·002 per cent.; Bi = 0·0007 per cent.; Cu = 0·0004 per cent.; Fe = 0·002 per cent.; Ag = nil; S = 0·001 per cent.

take place in the dissolved state, and to study this they added copper stearate in their experiments.

In connection with this we remark that a solution of copper during our experiments is quite possible, as a certain corrosion of the metal was observed. Yet we experienced no influence on the reaction velocity. It may be possible that an influence exists if one adds such compounds as copper stearate. However, it is good to realize that in this case a strange substance (stearate) is introduced into the system so that the phenomenon of induced oxidation is not excluded.

As long as no certainty exists with regard to the absence of induced oxidation, we consider the addition of soluble organic metal compounds for the study of specific metal action to be incorrect.

Rotterdam, Laboratory for Fuel and Oil Research.
Utrecht, Physical Laboratory of the University.

References.

[1] Leendertse, Vlugter, Waterman, and Van Westen, *J. Inst. Petrol. Tech.*, 1935, **21**, 661, 701; 1939, **24**, 16.
[2] "Beitrage zur Kentnis der negativen Katalyse im homogenen System," *Z. Phys. Chem.*, 1903, XLV, 641.
[3] C. Janssen, *Czn. Arch. f. Elektrotechn.*, 1930, **25**, 567. L. S. Ornstein, C. Krijgsman, and D.Th. J. ter Horst, *Physica*, 1935 (II), **3**, 201.
[4] "Ueber Schienbar umkehrbare photochemische Vorgänge und photochemischen Uebertragungs-katalyse," *Z. Phys. Chem.*, 1908, LXI, 513.
[5] *Rec. Trav. chim. Pays-Bas.*, 1925, XLIV, 1.
[6] *Physica*, 1932 (II), 322.
[7] J. L. Hiddink, Thesis. Utrecht, 1932. L. S. Ornstein, D.Th. J. ter Horst, and G. H. Frederik, *Proc. Kon. Acad. Amsterdam*, 1936, XXXIX, 325.
[8] *J. Inst. Petrol. Tech.*, 1937, **23**, 253.
[9] *Phys. Z.*, 1928, **29**, 683.
[10] Ornstein, Janssen, Krijgsman, and ter Horst, *loc. cit.*
[11] Titoff, *loc. cit.*
[12] *Chim. Ind.*, 1927, **18**, 3; *Premier Congrès de la Sécurité aérienne*, 1931, **1**, 55; *Bull. Soc. d'Encourag. à l'Ind. Nat., fevrier*, 1934.
[13] E. Vellinger and N. Saito, "2e Congrès Mondial du Pétrole," Paris, juin, 1937.

THE BLENDING OCTANE NUMBERS OF FURAN AND FURFURYL ALCOHOL.*

By Hugh B. Nisbet, D.Sc., Ph.D., F.I.C., F.R.S.E.

Summary.

Furan. Furan was added in various concentrations to motor spirit blends of different octane numbers, and it was found that in blends of low octane number the addition of small proportions of furan caused a big rise in octane number. This relative rise decreased with increasing proportions of furan, until when 30 per cent. was reached the rise became negligible.

The addition of furan to blends of high octane number caused only a slight increase in octane number, and when added to commercial *iso*-octane, a decrease in octane number was observed.

Furfuryl Alcohol. Owing to the insolubility of furfuryl alcohol in motor spirit of an aliphatic nature, the investigation was limited to the comparison of the blending values of furfuryl and ethyl alcohols in 10 per cent. blends in spirit containing benzole. The blending octane numbers of furfuryl alcohol in these blends are not as high as those of ethyl alcohol.

Introduction.

From the information which has been made available recently regarding the blending octane numbers of hydrocarbons and other compounds it has become apparent that this property is improved when (1) the molecule of an aliphatic hydrocarbon is highly centralized, (2) in addition to centralization in the open-chain hydrocarbon molecule there are also present one or more unsaturated linkages, (3) cyclic hydrocarbons contain unsaturated linkages and when the nature of the cyclic hydrocarbon becomes fully aromatic. It is also known that certain alcohols, particularly the lower aliphatic compounds, and also some ethers—*e.g.*, *iso*propyl ether—possess high-blending octane numbers (Table I).

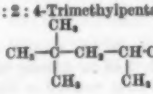
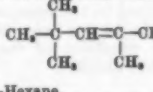
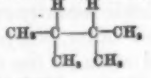
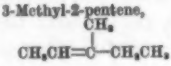
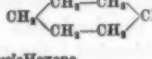
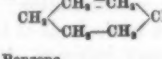
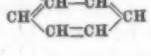
It has also been stressed, however, that the blending octane number of a compound is useless if no mention is made of the basis-fuel and the quantity in which the compound in question is blended,[7] for the anti-knock effect of added compounds is not linear with concentration. Moreover, the blending octane number is not the same in basis-fuels of low and high initial octane numbers. Indeed, this value may increase, decrease, or be fairly constant with increasing proportions of the blending agent (Curves *A*, *B*, and *D* respectively, Fig. 1). It may be low in blends with fuels of low octane number and high in blends with fuels of high octane number (Curves *A* and *C*, Fig. 1), or, vice versa, high in blends with fuels of low octane number and low in blends with fuels of high octane number (Curves *E* and *F*, Fig. 2).

In the present investigation the effect of combining a ring structure containing conjugated double bonds with an ether linkage as found in the molecule of furan (I), and the combination of this structure with an

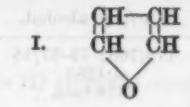
* Paper received 3rd February, 1941.

TABLE I.

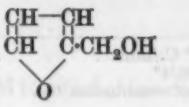
Blending Octane Numbers of Certain Hydrocarbons, Alcohols, and Ethers.

No.	Compound.	Blending octane number.	Conditions.	Ref.
1	n-Octane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	−19	Approx. 20 per cent. in fuel of octane number approx. 50; 212° jacket temp.	1
2	2 : 2 : 4-Trimethylpentane, 	100	,, ,, ,, ,,	1
3	1-Octene, $CH_2{=}CHCH_2CH_2CH_2CH_2CH_2CH_3$	25	,, ,, ,, ,,	2
4	4-Octene, $CH_3CH_2CH_2CH\ CHCH_2CH_2CH_3$	91	,, ,, ,, ,,	2
5	2 : 2 : 4-Trimethyl-3-pentene, 	144	,, ,, ,, ,,	2
6	n-Hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$	29	,, ,, ,, ,,	1
7	2 : 3-Dimethylbutane, 	124	,, ,, ,, ,,	1
8	1-Hexene, $CH_2{=}CHCH_2CH_2CH_2CH_3$	85	,, ,, ,, ,,	2
9	2-Hexene, $CH_3CH{=}CHCH_2CH_2CH_3$	100	,, ,, ,, ,,	2
10	3-Methyl-2-pentene, 	100	,, ,, ,, ,,	2
11	*cyclo*Hexane, 	85·5		3
12	*cyclo*Hexene, 	101·5		3
13	Benzene, 	101[a]	(*a*) 20 per cent. blend in *A*2, octane number 48·4; 212° jacket temp.; ethyl gasoline 8.30 engine.	4a
		87·5[b]	(*b*) 20 per cent. blend in spirit of octane number 70, C.F.R. Motor Method.	4b
14	Ethyl alcohol, CH_3CH_2OH	154	15 per cent. blend in fuel of octane number 63; C.F.R. Motor Method.	5
15	*iso*Propyl ether, $[(CH_3)_2CH]_2O$	105	20 per cent. blend in fuel of octane number 70; C.F.R. Motor Method.	6

alcoholic group, as in furfuryl alcohol (II), on the octane blending number has been studied from various angles.



I.



II.

Preparation of Furan and Furfuryl Alcohol.

Furoic acid and furfuryl alcohol were prepared from furfuraldehyde by Cannizaro's reaction.[12] The alcohol obtained was distilled under reduced pressure and had b. p. 75–77°/15 mm.

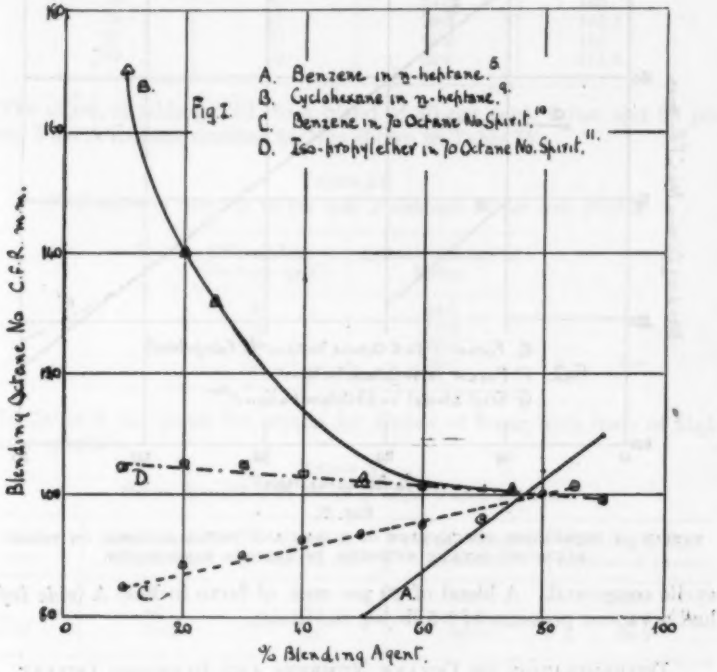


Fig. 1.

EFFECT OF VARYING PERCENTAGE IN BLENDS ON BLENDING OCTANE NUMBER FOR VARIOUS BLENDING AGENTS.

The furoic acid was decarboxylated following the method of Gilman and Louisinian,[13] substituting diethanolamine for the heavy coal-tar bases used in the original method when equally good results were obtained. The furan obtained had b. p. 31–35°, and was freshly distilled to remove any gum before being used in the engine tests. Table II gives the physical constants of furan and furfuryl alcohol taken from the literature.

TABLE II.

Physical Constants of Furan and Furfuryl Alcohol.

	Furan.	Furfuryl alcohol.
B. p. ° C./mm. . . .	31/745	170/760; 75–77/15
S.G. 20/4° . . .	0·9366	1·1285
Heat of combustion *Cp.* .	5001 cals.	6128 cals.

The volatility and high specific gravity made it impossible, owing to carburation difficulties, to determine accurately the octane numbers of furan itself * or of blends containing more than 50 per cent. of the hetero-

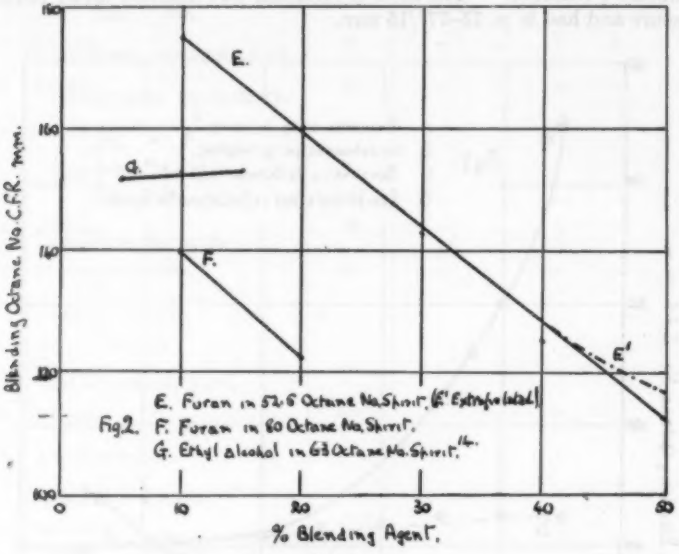


Fig. 2.

EFFECT OF INCREASING PERCENTAGE OF FURAN AND ETHYL ALCOHOL ON THEIR BLENDING OCTANE NUMBERS, IN VARIOUS BASIS FUELS.

cyclic compound. A blend of 20 per cent. of furan in Fuel A (*vide infra*) had a vapour pressure of 8·5 lb./sq. in. (Reid).

DETERMINATION OF OCTANE NUMBERS AND BLENDING OCTANE NUMBERS.

Octane numbers were determined by the C.F.R. Motor Method, using the following as reference fuels :—

Fuel	*A*	Octane No. 52·5	
,,	*B*	99·3	(Commercial *iso*-octane)
,,	*C*	80	(A blend of 60 per cent. *A* and 40 per cent. *B*)
,,	*D*	68·7	(Pool spirit containing benzole)
,,	*E*	69·8	(A blend of 40 pts. benzole and 50 pts. *A*)

* Furan was found to have an octane number of the order of 90.

Blending octane numbers were calculated using the formula of Garner, Evans, Sprake, and Broom.[14]

Results.

Furan.

Table III gives the results for furan added to a fuel of low octane number.

TABLE III.

Furan Blended with Fuel A.

Furan added, %.	Fuel *A* added, %.	Octane number of blend.	Blending octane number of furan.
10	90	64·7	174·5
20	80	74·0	160
30	70	79·5	142·5
40	60	81·5	125
50	50	82·0	111·5

The effect of adding TEL to a blend of 10 per cent. furan and 90 per cent. Fuel A (octane number 64·7) is shown in Table IV.

TABLE IV.

TEL added to Blend of 10 *per cent. Furan and* 90 *per cent. Fuel* A.

TEL added, mls./imp. gall.	Octane number of blend.
0	64·7
1	71·8
2	76·0
3	79·5

In Table V are given the results for blends of furan with fuels of high octane number.

TABLE V.

Furan Blended with Fuels of High Octane Number.

Basis fuel.	Octane number of basis fuel.	Furan in blend, %.	Octane number of blend.	Blending octane number of furan.
Fuel *C* .	80	10	86·0	140
,, .	80	20	88·5	122·5
Fuel *B* .	99·3	20	96·5	85·3

The values given in the Tables indicate that furan has a very high blending octane number when added in small percentages to a fuel of very low octane number (Curve *E*, Fig. 2), but that the relative rise in octane number of blends decreases with increasing proportions of furan, until when 30 per cent. of furan has been added the rise becomes negligible. The experimental values for blends of 40 per cent. and 50 per cent. furan with Fuel *A* are probably low due to carburation difficulties. It is possible that the extrapolated figures indicated in Curve *E'* more truly represent the blending octane numbers of furan in these blends.

The blending octane number of furan falls rapidly as the octane number of the blending fuel is raised (Curve *H*, Fig. 3). The blending octane numbers of furan in 20 per cent. blends with Fuels *A* and *C* are higher than most of those recorded for the compounds in Table I, and in Fig. 2 it is clearly shown that with fuels of low octane number furan is a better blending agent than ethyl alcohol in corresponding percentages, when considered from this aspect. In the blends with fuels of octane number 52·5 and 80 (Fuels *A* and *C*, respectively) which have been examined the

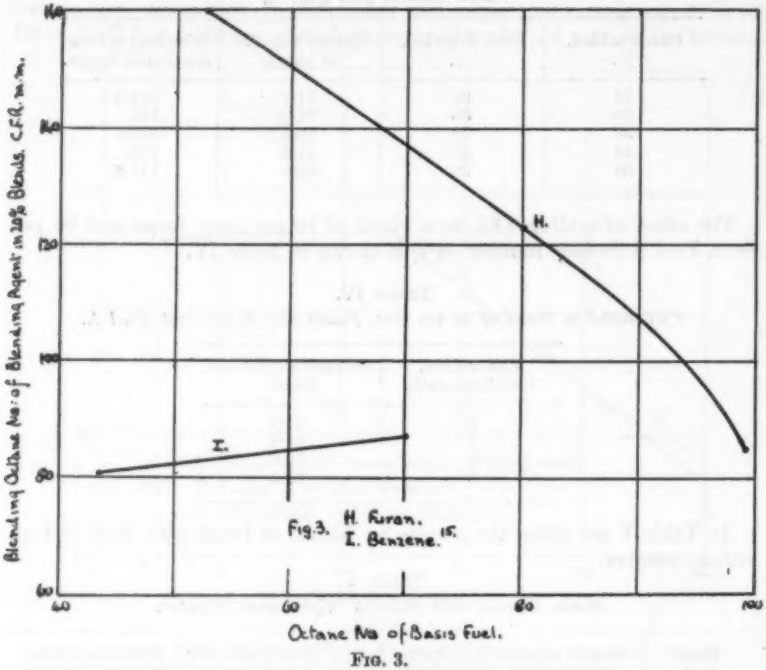


FIG. 3.

EFFECT ON BLENDING OCTANE NUMBERS, OF BLENDING FURAN AND BENZENE IN 20% WITH BASIS FUELS OF DIFFERENT OCTANE NUMBERS.

blending octane number of furan is higher than that of *iso*propyl ether when used in blends with spirit of octane number 70 (Curves *D*, *E*, and *F*, Figs. 1 and 2). A 10 per cent. blend of furan with Fuel *A* shows quite a good response to TEL—comparable, indeed, with the responses of other blends of somewhat similar composition. This is brought out in Fig. 4, in which it is to be noted the results plotted are for mls./imp. gallon for the furan blend and mls./Amer. gallon for the other blends, and so are slightly adverse to furan.

Furfuryl Alcohol.

At the outset it was found that furfuryl alcohol was not completely miscible with motor spirit. It did not mix at all with Fuel *A*, and only

approximately 16 per cent. could be dissolved in Fuel *D*, which contained benzole.

The investigation was limited, therefore, to a comparison of the blending values of furfuryl alcohol and ethyl alcohol in 10 per cent. blends in Fuels *D* and *E*. The results are indicated in Table VI, and show that furfuryl alcohol is slightly inferior to ethyl alcohol in these blends.

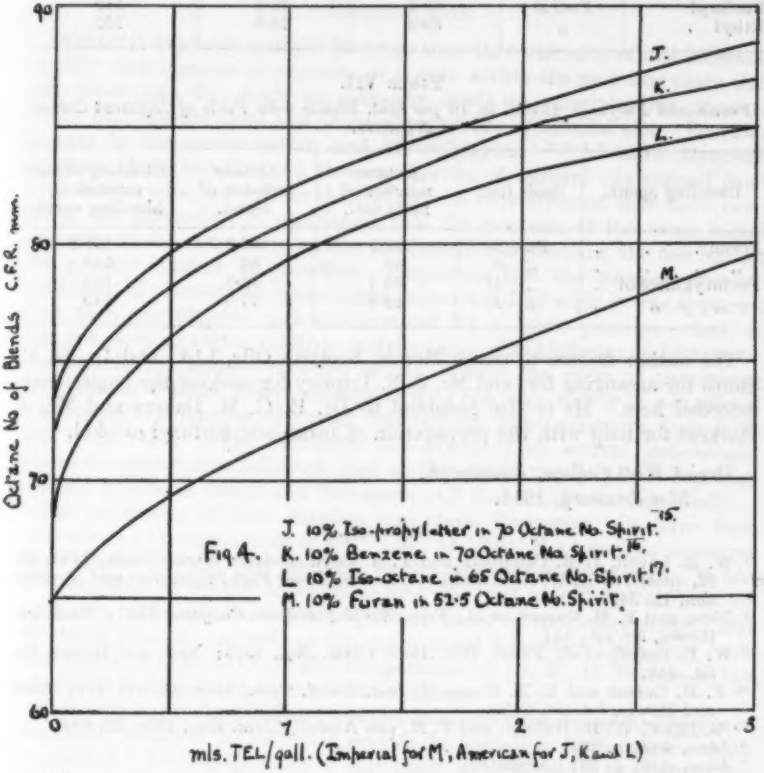


Fig 4.

FIG. 4.

EFFECT OF ADDITION OF TEL TO 10% BLENDS OF SEVERAL BLENDING AGENTS IN VARIOUS BASIS FUELS.

In addition, it is interesting to note the relationship between the blending octane numbers of furan and furfuryl alcohol in 10 per cent. blends with various basis fuels as shown in Table VII. Although both furan and furfuryl alcohol show high blending octane numbers in these blends, in view of the difference in the nature and octane numbers of the basis fuels it is not possible to reach any conclusion as to the effect on the blending value of introducing the alcoholic group $-CH_2OH$ into furan.

TABLE VI.

Furfuryl Alcohol and Ethyl Alcohol in 10 per cent. Blends with Fuels containing Benzole.

Blending alcohol.	Basis fuel.	Octane number of basis fuel.	Octane number of blend.	Blending octane number of alcohol.
Furfuryl .	Fuel *D*	68·7	72·2	104
Ethyl . .	,,	68·7	74·5	127
Furfuryl .	Fuel *E*	69·8	77·0	142
Ethyl . .	,,	69·8	78·0	152

TABLE VII.

Furan and Furfuryl Alcohol in 10 per cent. Blends with Fuels of Different Octane Numbers.

Blending agent.	Basis fuel.	Octane number of basis fuel.	Octane number of blend.	Blending octane number of blending agent.
Furan . . .	Fuel *A*	52·5	64·7	174·5
,, . . .	,, *C*	80	86	140
Furfuryl alcohol .	,, *D*	68·7	72·2	104
,, ,, .	,, *E*	69·8	77·0	142

The author desires to thank Messrs. Scottish Oils, Ltd., and Dr. G. H. Smith for arranging for, and Mr. J. S. Tripney for making the engine tests recorded here. He is also indebted to Dr. R. G. M. Dakers and Mr. J. Harkess for help with the preparation of furan and furfuryl alcohol.

Heriot Watt College, Edinburgh,
31st January, 1941.

References.

[1] W. E. Lovell, J. M. Campbell, and T. A. Boyd, *Industr. Engng Chem.*, 1931, **23**, 26, quoted by A. W. Nash and D. A. Howes, *Motor Fuel Preparation and Application*, **11**, 341.
[2] *Idem*, and F. H. Garner, *et al.*, *Proc. World Petroleum Congress*, 1933; Nash and Howes, *loc. cit.*, 344.
[3] W. E. Lovell, *et al.*, *Petrol. Div. Amer. Chem. Soc.*, 1933; Nash and Howes, *loc. cit.*, 349.
[4a] F. H. Garner and E. B. Evans, *J. Inst. Petrol. Tech.*, 1932, **18**, 751–778; Nash and Howes, *loc. cit.*, 347.
[4b] G. Egloff, W. H. Hubner, and P. M. van Arsdell, *Chem. Rev.*, 1938, **22**, 244.
[5] *Idem*, *ibid.*, p. 262.
[6] *Idem*, *ibid.*, p. 237 (calculated).
[7] J. Smittenberg, H. Hoog, B. H. Moerbeek, and M. J. van den Zijden, *J. Inst. Petrol.*, 1940, **26**, 303.
[8] *Idem*, *ibid.*, p. 300.
[9] *Idem*, *ibid.*, p. 301.
[10] G. Egloff, *et al.*, *loc. cit.*, p. 244.
[11] *Idem*, *ibid.*, p. 237.
[12] "Organic Syntheses," VI, 44.
[13] H. Gilman and M. B. Louisinian, *Rec. trav. chim.*, 1933, **52**, 156.
[14] F. H. Garner, E. B. Evans, C. H. Sprake, and W. G. T. Broom, *Proc. World Petroleum Congress*, 1933; Nash and Howes, *loc. cit.*, p. 340.
[15] G. Egloff, *et al.*, *loc. cit.*, p. 262.
[16] *Idem*, *ibid.*, pp. 232, 244.
[17] *Idem*, *ibid.*, p. 237.
[18] *Idem*, *ibid.*, p. 244.
[19] *Idem*, *ibid.*, p. 234.

THE VISCOSITY OF RUSSIAN AND RUMANIAN LUBRICATING OILS AT HIGH PRESSURE.*

By R. B. Dow, J. S. McCartney, and C. E. Fink.

Introduction.

While it has been realized for some time that viscosity of oils increases rapidly with increase of pressure, it is only within the past few years that any laboratory has made an intensive study to correlate this pressure effect with the chemical and physical properties of mineral oils. Previous reports by the senior author and his colleagues [1, 2, 3, 4, 5] have discussed pressure characteristics and these properties of mineral oils refined from American crudes, as well as the methods of measurement that have been used. In particular, it was found that for two oils of the same initial viscosity at the same temperature at atmospheric pressure, the one having the greater content of paraffinic compounds had the smaller pressure coefficient of viscosity at some higher pressure. But while it was apparent that high paraffinicity was accompanied by a lower pressure effect, it was not clear as to the relative contributions of naphthenic and aromatic compounds for greater pressure effects. Since the ratio of percentage composition of these latter compounds does not vary widely in oils refined from American sources, the need was felt for more extensive tests with oils from other fields. Through the kindness of several individuals, whose co-operation is acknowledged at the end of this paper, it has been possible to obtain samples of European and Asiatic oils for this study.

The viscosities of four Russian and three Rumanian oils have been determined at temperatures of 100°, 130°, and 210° F. at various pressures up to 46,000 lb./in.^{2}. In addition to the viscosity measurements, it has been possible to obtain other important physical and chemical data for these oils. These include the important items of molecular weight and structural analysis, as well as the more usual inspection data that have been made possible through the co-operation of Dr. M. R. Fenske of the Petroleum Refining Laboratory of this College.

It is necessary, for obvious reasons, that information as to the exact geographic location of refineries and facts regarding trade names must be omitted. For the purpose of this paper it is sufficient to identify the oils by number, and to state that they are typical, conventionally refined oils from crudes of the well-known fields of Russia and Rumania. Some data on the refining processes as given by the respective contributors of the samples will be included with the chemical and physical properties that have been studied by the authors.

Data at Atmospheric Pressure.

No details of the refining process for the Russian oils have been furnished to the authors, but the contributor characterized them as typical

* Paper received 23rd January, 1941.

of the more important oils of that country. The Rumanian oils are typical lubricating oils obtained from non-paraffinic crudes by vacuum distillation. The distillate was neutralized with caustic soda and then vacuum redistilled into cuts. Sample 1 is a first-cut spindle oil; sample 2 is a more viscous cut, and sample 3 is a cylinder oil which remained as bottoms after the fractionating process was completed. Samples 1 and 2 were conventionally treated with sulphuric acid and then neutralized with caustic soda.

Table I is a summary of the tests and subsequent computations made for the oils at atmospheric pressure. These include the conventional

TABLE I.

Data on Russian and Rumanian Oils at Atmospheric Pressure.

Origin:	Russia.	Russia.	Russia.	Russia.	Rumania.	Rumania.	Rumania.
Oil No.:	"00."	"1."	"2."	"B.S."	"1."	"2."	"3."
Gravity A.P.I.	27·1	24·0	25·4	24·6	20·9	17·3	15·6
Sp. gr. 60/60° F.	0·9234	0·9101	0·9020	0·9064	0·9283	0·9509	0·9621
Density, 100° F.	0·9085	0·8952	0·8869	0·8914	0·9133	0·9360	0·9474
" 130° F.	0·8980	0·8846	0·8765	0·8809	0·9029	0·9257	0·9370
" 210° F.	0·8711	0·8573	0·8489	0·8534	0·8761	0·8993	0·9108
Viscosity (c.s.) 100° F.	200·70	99·30	37·53	258·40	23·09	486·40	1731·0
" 130° F.	74·50	41·30	18·50	188·00	11·90	142·00	403·6
" 210° F.	12·92	5·85	5·19	28·82	3·69	17·22	35·39
Viscosity index	38	49	66	84	35	−36	−25
A.S.T.M. pour point, ° F.	+5	−15	−25	+20	−25	+30	+40
A.S.T.M. colour	7½	3	2½	7½	4½	5½	black
Aniline point, ° C.	92·2	94·3	88·0	120·1	60·8	77·8	80·4
Refractive index, 20° C.	1·5084	1·4993	1·4959	1·4983	1·5167	1·5263	1·5365
Molecular weight	435	393	364	666	285	409	511
Rings per molecule	3·13	2·75	2·48	3·40	2·18	3·45	4·05
n in $C_nH_{(2n-z)}$	31·7	28·5	26·4	48·1	20·9	30·0	37·7
z in $C_nH_{(2n-z)}$	8·4	6·0	6·0	7·9	7·5	11·3	16·2
Paraffins, per cent.	58	59	60	70	54	51	53
Naphthenes, per cent.	30	33	30	24	24	29	21
Aromatics, per cent.	12	8	10	6	22	20	26

density and viscosity measurements (kinematic) made with 5-c.c. pycnometers and modified Ostwald pipettes, respectively, at the given temperatures. Viscosity index was computed from:

$$\text{V.I.} = \frac{(100^\circ\text{ F. vis. of 0 V.I. oil}) - (100^\circ\text{ F. vis. of unknown oil})}{(100^\circ\text{ F. vis. of 0 V.I. oil}) - (100^\circ\text{ F. vis. of 100 V.I. oil})} \times 100$$

by means of conventional tables for the viscosities of the 100 and 0 V.I. oils, *e.g.*,[6]. The A.S.T.M. calculations require no explanation. The computations for structural characteristics were made after the manner of Waterman and his associates.[7]

HIGH-PRESSURE MEASUREMENTS.

The viscosities of the four oils were measured at pressures ranging from atmospheric to 46,000 lb./in.^{2} in a modified form of the rolling-ball viscometer of Hersey.[8] The theory of the viscometer is quite simple, viscosity being determined from the time of roll of a ball down a tube inclined at a small angle to the horizontal. The roll time can be observed with a high degree of accuracy by any of the well-known methods of

measuring time intervals that vary from a few seconds to 10 or 15 minutes. But for short roll times the viscosity is not simply related to them; also, since the roll time depends on other variables, such as ratio of diameter of bore to diameter of ball, it is evident that the viscometer must be calibrated for every change of geometry and of tube. Hersey [9] resorted to dimensional analysis to find the proper combinations of variables. But if the same tube be used, and a calibration curve determined for each change of ball diameter and angle of roll—the conditions under which the instrument is used by the authors—it is possible to find a simple relation from first principles between roll-time and viscosity.

Considering the motion of the ball to be one of rotation only about the instantaneous axis, the gravitational torque is:

$$\rho_0 Vgr \sin \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ_0 = density of ball, V = volume of ball, r = radius of ball, g = accel. due to gravity, θ = angle of inclination to horizontal.

The opposing torque due to buoyancy is

$$\rho Vgr \sin \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ρ = density of liquid.

The opposing torque required to change the angular momentum of the liquid will be denoted by L; it is impossible to evaluate it uniquely.

For uniform motion down the tube, the resultant of these torques must be balanced by the viscous torque

$$\mu\left(\frac{L'}{T}\right) f\left(\frac{A}{d}\right) r \sin \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where μ = coefficient of viscosity, L' = length of roll-path, T = roll-time. The functional relation $f\left(\frac{A}{d}\right)$, between effective area and thickness of film of liquid is also unknown.

Equating torques in the two directions of rotation, and substituting the constant K for the combination of V, g, L', and $f\left(\frac{A}{d}\right)$:

$$(\rho_0 - \rho) - L = K \frac{\mu}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

K can be considered to be constant over a wide range of experimental conditions. For example, a temperature change of 212° F. causes an error of only 0·2 per cent. in K, and a pressure change of 5000 atmospheres causes like error of 0·2 per cent.

For large values of T, L becomes negligible and a linear relation exists between $T(\rho_0 - \rho)$ and μ. For short values of T, L becomes appreciable and it becomes necessary to determine μ graphically from a calibration curve. Fig. 1 is a calibration curve for a 0·635-cm.-diameter ball in a tube of 1·072 cm. diameter at an approximate angle of 6·3°. It is the practice

of the authors to calibrate the viscometer for each ball diameter and angle of inclination, and then to compute μ from the slope of the linear portion of the curve, or to read it directly from the curve when the inertia effect is large enough to cause the curve to deviate from linearity.

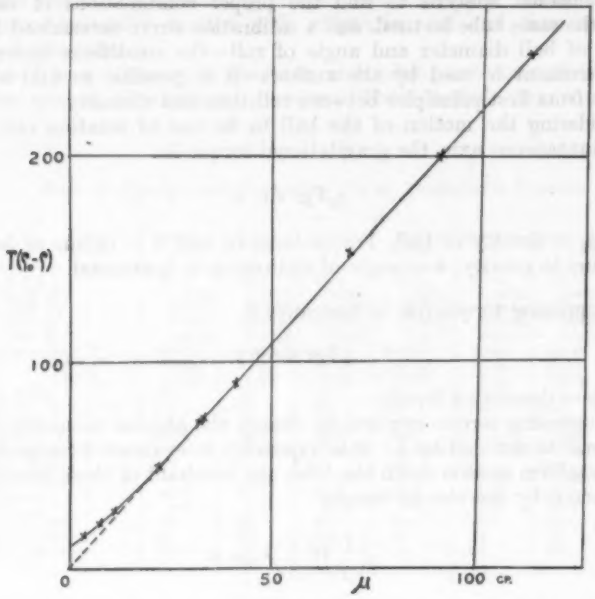


FIG. 1.

CALIBRATION CURVE FOR ROLLING-BALL VISCOMETER.

DATA AT HIGH PRESSURE.

The viscosity–pressure–temperature data for the seven samples are collected in Table II. The viscosities were computed from equation (4), as explained previously, by putting $L = 0$ for long roll times; or were read directly from the calibration curve when μ fell on a non-linear portion of the curve. Densities of the liquids at the various pressures and temperatures were computed from the equation of Dow and Fink.[10] Pressures were measured by means of a manganin gauge coil that was inserted in the pressure line connecting to the viscometer. The change of resistance is known to bear a linear relation to change of pressure,[11] and the method of calibration against a dead-weight gauge is done according to standard procedure. Corrections for initial acceleration of the ball and change of path length were made as previously described (1). The other corrections are negligible for the pressure and temperature ranges that have been used.

TABLE II.

Viscosity–Pressure Data.

Viscosity in centipoises.

Pressure in lb./in.².	Russian "00."	Russian "1."	Russian "2."	Russian "Bright Stock."	Rumanian "1."	Rumanian "2."	Rumanian "3."
			100° F.				
14·3	180	91	32	512	21	453	No data
1000	230	112	37	590	24	595	
2000	285	133	45	705	28	780	
3000	355	161	54	855	33	1010	
4000	435	195	65	1030	39	1330	
5000	529	255	76	1245	46	1725	
6000	642	283	91	1505	54	2230	
7000	788	340	107	1820	63	2905	
8000	940	410	125	2190	74	3810	
9000	1160	490	148	2610	87	5010	
10×10^3	1410	590	174	3130	103	6520	
12	2090	845	240	4750	142		
14	3090	1210	333		197		
16	4900	1740	452		270		
18		2460	610		370		
20		3490	840		509		
22			1160		703		
			130° F.				
14·3	67	35	16	174	11	135	383
1000	80	42	18	200	12	160	490
2000	97	50	21	240	14	200	630
3000	118	60	24	280	16	250	795
4000	140	70	27	332	18	310	1000
5000	168	83	31	396	21	390	1265
6000	201	97	36	468	24	495	1590
7000	240	114	41	550	28	630	2005
8000	289	135	48	650	32	790	2510
9000	340	159	55	765	37	990	3170
10×10^3	400	187	64	900	42	1225	3990
12	548	255	86	1230	55	1900	6310
14	760	350	112	1670	72	2980	9940
16	1070	478	149	2250	95	4700	
18	1500	650	195	3010	125	7340	
20	2070	885	253	4000	164		
22	2880	1200	329	5340	215		
24	4060	1600	429		283		
26	5470	2300	555		371		
28		3150	715		492		
30			930		652		
32			1195		861		
34			1535				
36			2000				
			210° F.				
14·3	12	8	4	25	4	16	32
1000	13	9	5	28	4	18	38
2000	158	10	5	32	5	21	44
3000	17	11	6	37	5	24	52
4000	20	13	6	43	5	28	63
5000	23	15	7	49	6	33	74
6000	26	17	8	56	6	38	87
7000	6429	19	9	64	6	44	102
8000	33	21	10	73	7	51	120
9000	37	23	11	82	8	59	142

TABLE II—*continued.*

Viscosity in centipoises.

Pressure in lb./in.².	Russian "00."	Russian "1."	Russian "2."	Russian "Bright Stock."	Rumanian "1."	Rumanian "2."	Rumanian "3."
10×10^3	41	26	12	93	9	69	168
12	52	33	15	116	10	94	231
14	67	41	19	145	12	128	314
16	85	51	23	190	15	175	423
18	107	64	27	236	19	238	592
20	132	80	32	290	23	320	790
22	170	101	39	360	27	430	1070
24	221	129	46	450	32	575	1470
26	283	160	56	545	38	770	1990
28	357	194	68	670	46	1050	2680
30	445	237	82	830	56	1420	3630
32	555	289	100	1020	68	1930	4899
34	690	354	120	1240	82	2610	6550
36	863	444	143	1520	100	3530	
38	1085	562	170	1850	120	4800	
42	1690	840	244	2720	172		
46	2620	1170	352	3950	243		

The equation relating viscosity to pressure is not known accurately. It has been proposed by several investigators that

$$\mu = \mu_0 e^{ap} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where μ_0 is the coefficient of viscosity at a certain temperature at atmospheric pressure. Differentiation of (5) shows that a equals the pressure coefficient of viscosity, considered to be constant. However, a is but an approximation, holding exactly in no case; at low pressures a departs noticeably from constancy.

The data of this paper, as well as many other, fit the following relation more accurately

$$\mu = C\mu_0^{ap} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

at all three temperatures.

Likewise, the relation between viscosity and temperature is not known exactly, although empirical relations such as the log log chart of the A.S.T.M., for example, are quite accurate over a moderate temperature range at atmospheric pressure. Since only three temperatures were used in this investigation, no attempt has been made to correlate the temperature characteristics of viscosity.

The data of Table II at 100° and 210° F. have been used to compute the constant a of equation (6), and the curves at 210° are shown in Fig. 2, in which the ratio of the common logarithms of the viscosity under pressure to the viscosity at atmospheric pressure is plotted against pressure.

The average slopes of the curves at 100° and 210° are given in Table III.

Table IV contains the average temperature coefficient of viscosity computed between 100° and 210° F. for constant pressures of 1000, 10,000, and 20,000 #/in.².

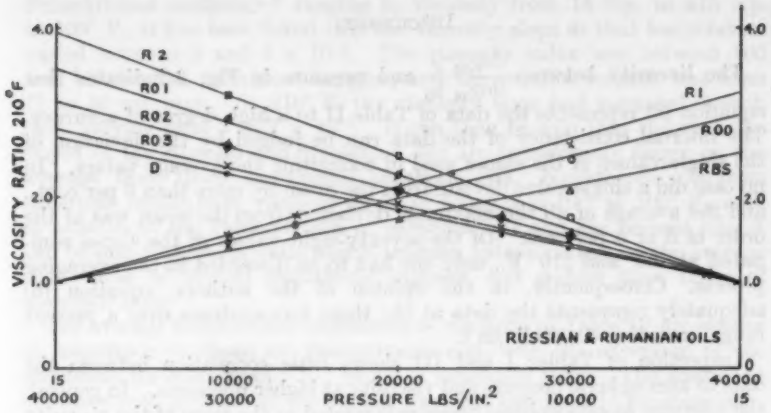


FIG. 2.

RATIO OF THE COMMON LOGARITHMS OF THE VISCOSITY UNDER PRESSURE TO THE VISCOSITY AT ATMOSPHERIC PRESSURE PLOTTED AGAINST PRESSURE.

TABLE III.

Average Slope of Viscosity Curves at 100° and 210° F.

Oil.	Slope $\times 10^5 = 1/p\left(\frac{\log_{10}\mu}{\log_{10}\mu_0} - 1\right)$.	
	100° F.	210° F.
Russian "00" . . .	4·10	4·80
" "1" . . .	4·17	5·50
" "2" . . .	4·92	7·64
" "BS" . . .	2·81	3·79
Rumanian "1" . . .	5·11	6·29
" "2" . . .	4·38	5·26
" "3" . . .	—	4·65

TABLE IV.

Mean Temperature Coefficient of Viscosity between 100° and 210° F.

Oil.	$\frac{1}{\mu_{100}}\left(\frac{\partial\mu}{\partial\tau}\right)_{1000} \times 10^5$.	$\frac{1}{\mu_{100}}\left(\frac{\partial\mu}{\partial\tau}\right)_{10,000} \times 10^5$.	$\frac{1}{\mu_{100}}\left(\frac{\partial\mu}{\partial\tau}\right)_{20,000} \times 10^5$.
Russian "00" .	858	883	—
" "1" .	836	869	888
" "2" .	786	847	875
" "BS" .	866	882	—
Rumanian "1" .	758	830	868
" "2" .	882	900	—
" "3" * .	1153	1197	—

* Between 130° and 210° F.

Discussion.

The linearity between $\frac{\log_{10} \mu}{\log_{10} \mu_0}$ and pressure in Fig. 2 indicates that equation (6) represents the data of Table II to a high degree of accuracy. The internal consistency of the data can be judged by the deviation of the single values of the slopes used in computing the average values. In no case did a single value deviate from the mean by more than 9 per cent., and the average of all the maximum deviations from the mean was of the order of 5 or 6 per cent. Of the seventy-eight values of the slopes computed at 100° and 210° F., only one had to be discarded in the averaging process. Consequently, in the opinion of the authors, equation (6) adequately represents the data at the three temperatures over a present range exceeding 40,000 lb./in.^{2}.

Inspection of Tables I and III shows little correlation between the data at atmospheric pressure and viscosity at higher pressures. In general, the viscosity at atmospheric pressure is related to the slope of the viscosity line in that they increase or decrease inversely but not uniformly. For example, Rumanian "1" at 100° and 210° F., as well as at 130° F., has the smallest initial viscosities but the greatest slopes. There appears to be little direct relation between viscosity index and the pressure effect. This is not unexpected, since it is realized that this quantity has little absolute significance by virtue of its definition,[6] although it is applied commonly in the oil industry for comparison purposes. There is good correlation between viscosity slope and molecular weight, and some correlation with number of "rings per molecule," but due to deviations from smooth curves, as well as lack of sufficient data, it is impossible to find mathematical correlation for these data.

It has previously been mentioned that oils of higher paraffinic composition have lower relative viscosities under pressure, and that the relative contributions of naphthenic and aromatic compounds towards higher viscosity have not been determined. The Waterman data of Table I bear out these conclusions regarding paraffinicity, as it can be seen that the viscosity slopes for the four Russian oils are less than those for the Rumanian oils at 100°, although it is interesting to note that the distinction is not so clear at the higher temperature. It is to be noted in this respect that the viscosity slope at both temperatures for Russian "Bright Stock" is the smallest of those given in Table III. It is disappointing to observe that the effects of naphthenes and aromatics cannot be separated in these cases. The sum of the two is practically the same for the Russian samples, and there is no noticeable difference in the viscosity slopes at 100° except for "Bright Stock," which has a high relative paraffin content. Likewise for the Rumanian samples, any possible separation of these effects is not valid, since the oils have lower paraffinic content. The authors hope to throw additional light on this interesting question in a further communication which will discuss the viscosity characteristics of Burma oils.

Since the properties of Pennsylvania oils have been studied intensively by the authors, it may be of interest to compare the viscosity–pressure–temperature characteristics of them with the present oils. For seven

Pennsylvania samples,[1,3] ranging in viscosity from 14 c.p. to 415 c.p. at 100° F., it has been found that the viscosity slope at that temperature varied between 2 and 4 $\times$ 10^{-5}. The viscosity index was between 100 and 127 for the individual samples, and the paraffin content was from 77 to 80 per cent. At 210° F. the viscosity slope had increased in each case, varying from 3 to 7 $\times$ 10^{-5}. It can then be seen that the viscosity slopes of the Russian and Rumanian oils are considerably larger on the average than those for typical paraffinic oils. Naphthenic oils from American crudes have viscosity slopes of about 5 $\times$ 10^{-5} at 100° F., and, in relation to the Pennsylvania or paraffinic oils and the present oils, it can be said that the Russian and Rumanian values are less on the average than those of typical naphthenic samples, but greater than those of paraffinic ones.

The average temperature coefficients of viscosity of Table IV are similar in magnitude to those for Pennsylvania oils, with the exception of the coefficient for Rumanian "3," which is unusually large. The coefficient increases with pressure in the normal way, but non-linearly for these oils.

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References.

[1] R. B. Dow, "Pressure and Temperature Effects on Viscosity of Oils," *J. appl. Physics*, 1937, **8**, 367.
[2] R. B. Dow, M. R. Fenske, and H. E. Morgan, "Pressure Effect on Viscosity of Oils and Diphenyls," *Industr. Engng Chem.*, 1937, **29**, 1078.
[3] R. M. Dibert, R. B. Dow, and C. E. Fink, "Viscosity of Pennsylvania Oils at High Pressure," *J. appl. Physics*, 1939, **10**, 113.
[4] B. W. Thomas, W. R. Ham, and R. B. Dow, "Viscosity–Pressure Characteristics of Oils," *Industr. Engng Chem.*, 1939, **31**, 1267.
[5] R. B. Dow, "Viscosity of Liquids at High Pressure," *Phil. Mag.*, 1939, **28**, 403.
[6] E. W. Dean and G. H. B. Davis, "Computation of Viscosity Index," *Chem. and Met.*, 1929, **36**, 618; G. H. B. Davis, M. Lapeyrouse, and E. W. Dean, *Oil Gas J.*, 1932, **30**, 92.
[7] J. C. Vlugter, H. I. Waterman, and H. A. Van Westen, "Structure Analysis of Oils," *J. Inst. Petrol. Tech.*, 1935, **21**, 661.
[8] M. D. Hersey and H. Shore, "Viscosity of Lubricants under Pressure," *Mech. Eng.*, 1928, **50**, 221.
[9] M. D. Hersey, "Rolling-ball Viscometer for High Pressures," *J. Wash. Acad. Sci.*, 1916, **6**, 525.
[10] R. B. Dow and C. E. Fink, "Density of Oils at High Pressure," *J. appl. Physics*, 1940, **11**, 353.
[11] P. W. Bridgman, "The Physics of High Pressure," Chap. 3. Macmillan, 1931.

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OBITUARY.

ANDREW CAMPBELL.

With the death of Andrew Campbell, which occurred at his home at Beckenham on 16th February, 1941, a great pioneer is lost to Petroleum Technology. Andrew Campbell had his roots in the Scottish shale industry, and all that was good in that industry he translated into petroleum practice.

Born in Edinburgh in 1868, Andrew Campbell gained his early experience as a chemist with the Linlithgow Oil Company, after serving his apprenticeship with the well-known Edinburgh City Analyst, Mr. I. Falconer King. At the age of twenty-one he joined the Burmah Oil Company as Assistant Chemist to that company, with whom he remained until 1913, and afterwards served as their Advisory Chemist. During his years with the Burmah Oil Company he was actively engaged in refinery management, and was always greatly interested in new developments. I remember with what keenness he watched over efforts to separate aromatic hydrocarbons from Iranian gasoline by means of liquid SO_2. He was, in effect, well ahead of most of his colleagues in the industry, reading widely and travelling extensively. It is of some interest to note that when he took charge of the Burmah Oil Company's original refinery at Dunneedaw the throughput was less than 1,000,000 gallons per month and the original scheme was for refined kerosine, jute batching oil, wax candles and coke. Before he retired from Burma he brought this figure up to over 14,000,000 gallons per month, divided between the Dunneedaw Refinery and the Company's new one at Syriam. He developed the original idea of Dr. Hood's bauxite refining method into a works process, and this is of interest, too, in view of the recent revival towards bauxite as an adsorbent in the United States of America. He took an active interest also in experiments, carried out on a semi-plant scale, of a pioneering cracking process called the Noad, owned by the Burmah Oil Company through a subsidiary company formed to develop it. However, the war of 1914–18 intervened, and by the end of it other, and more fully developed, processes seemed to make further experimenting scarcely worth while.

In 1908, because of the Burmah Oil Company's interest in what was to become the Anglo-Iranian Oil Company, he visited Iran and drew up plans for a refinery at Abadan for a throughput of 2,000,000 gallons monthly—a figure which was vastly increased even before erection began. After the last war he visited Rumania with a deputation of oil technologists for the assessment of war damage.

Still later he became the Managing Director of National Oil Refineries, Ltd., and in this capacity built and equipped the great refinery at Swansea.

Some of Andrew Campbell's aphorisms remain in my mind today, especially the one " distillation is the cheapest method of refining." How prophetic was that saying, and how likely it is to become more and more effective when one considers the isolation of special and particular " chemical bricks " from the crude oil !

Andrew Campbell was a founder member of the Institute and a member of Council from 1916 to 1926. His rather remarkable paper on refining, which was later expanded into a useful monograph, showed his interest in the subject and his lucidity as an expounder and his acumen in foreseeing future developments. In Council he was a very Nestor, sane in judgment, equally balanced in knowledge and wisdom. He was always kindly, courteous and helpful, especially to his younger colleagues. Very open-minded and always ready to give the freest scope to his associates, he was a veritable father to his flock. Personally, as one who came into the industry with merely an academic background, I feel I owe him more than I can express, and these few words are a heartfelt tribute to one of whom it can fairly be said, " He made men."

A. E. DUNSTAN.